Organic Carbon Sequestration in Soils: An Investigation of Five Profiles in Hesse, Germany

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List of Important Abbreviations

Alo	oxalate-extractable aluminium
AAS	atomic absorption spectroscopy
BDF	Boden-Dauerbeobachtungsfläche
BK	Bodenkundliche Kartieranleitung
CEC_{eff}	effective Cation Exchange Capacity
CEC_{pot}	potential Cation Exchange Capacity
Df	density of fluid (g cm^{-3})
Ds	density of solid (g cm^{-3})
DIN	Deutsches Insitut für Normung e.V. (German Insitute for Standardization)
EGME	ethylene glycol monoethyl ether
Fed	sodium-dithionite-citrate-bicarbonate-extractable iron
Feo	oxalate-extractable iron
G	gravitational acceleration (cm sec^{-2})
ISSS	International Society of Soil Science
ME	monolayer equivalent
Mno	oxalate-extractable manganese
OC	organic carbon
Pg	petagram (10^{15} g)
R	particle radius (cm)
rpm	rounds per minute
SSA	specific surface area
Tg	teragram (10^{12} g)
TOM	total organic matter
V	particle velocity (cm s-1)
Vf	fluid viscosity at temperature *t* (g cm^{-1} s^{-1})
XRD	x-ray diffraction
WRB	World Reference Base for Soil Resources

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Zusammenfassung

Untersuchungskontext

In dem Maß, in dem die klimatischen Auswirkungen von Treibhausgas-Emissionen immer deutlicher geworden sind, ist das wissenschaftliche Interesse an der Identifikation und Nutzung potenzieller Kohlenstoffsenken in den letzten Jahren immer größer geworden. Hintergrund dieses Interesses ist die Reduktion des atmosphärischen CO_2-Gehalts. Neben den bekannten Senken im marinen Bereich stehen zur Zeit auch terrestrische Kohlenstoffsenken, insbesondere Vegetation und Böden, im Fokus der Untersuchungen. Man vermutet, dass vor allem diese Senken für die 1,8 Pg yr^{-1} (Pg= Petagramm= 10^{15}) Kohlenstoff verantwortlich sind, die in Modellen des globalen Kohlenstoffkreislaufs pro Jahr nicht erklärt und zugerechnet werden können (Houghton et al. 1998). Obwohl bisher vor allem Waldbewirtschaftung und –management im Zentrum von politischen Strategien gestanden haben, werden nach dem Kyoto-Protokoll der UN-Konvention über den Klimawandel inzwischen auch Böden als ein Instrument betrachtet, um den Anstieg der CO_2-Konzentration in der Atmosphäre zu reduzieren (siehe Batjes 1999). Dies lässt sich speziell mit Artikel 3.4 des Kyoto-Protokolls in Verbindung bringen, in dem vorgeschlagen wird, dass „sources and removals by sinks in the agricultural soils and land-use change and forestry categories“ in Zukunft ebenfalls Berücksichtung finden sollen. Hierdurch ist eine Tür geöffnet worden, so dass Länder Böden als Senken bei der Berechnung der CO_2-Emissionen geltend machen können.

Obwohl Böden unzweifelhaft ein signifikanter Pool von Kohlenstoff sind, ist ihre Bedeutung als potenzielle langfristige Senke für atmosphärischen Kohlenstoff keineswegs klar. Unter der Voraussetzung, dass man ein effizientes Management und geeignete Maßnahmen ergreift, haben Böden zwar das Potenzial, eine wichtige Rolle bei der Verminderung der atmosphärischen CO_2-Konzentration zu spielen. Es ist jedoch problematisch, die Ergebnisse der großmaßstäbigen CO_2-Modelle als Basis zur Entwicklung einer globalen Strategie mit dem Ziel der Verringerung der CO_2-Konzentration zu verwenden. Dies liegt insbesondere daran, dass es in Bezug auf die geochemischen Mechanismen bei der Ablagerung von Kohlenstoff in Böden große Wissenslücken gibt. Hierdurch könnte die Implementierung entsprechender Strategien und Maßnahmen behindert werden. Im Ergebnis könnten noch größere Schäden entstehen. Als Konsequenz unterschiedlicher biologischer und

geochemischer Faktoren wie etwa der mineralogischen Zusammensetzung haben nicht alle Böden das gleiche Potenzial, um Kohlenstoff aufzunehmen und zu speichern. Allerdings hat der Einfluss von Bodentyp und Mineralogie auf die Kapazität von Böden, atmosphärischen Kohlenstoff zu fixieren, bisher nicht genügend Aufmerksamkeit erhalten. Trotz großer wissenschaftlicher Forschritte, die in den letzen Jahren in Bezug auf die Kohlenstoffdynamik in Böden erreicht worden sind, gibt es nach wie vor offene Fragen insbesondere hinsichtlich der spezifischen Mechanismen, die für die Stabilisierung und Ablagerung organischen Kohlenstoffs in Böden verantwortlich sind. Dabei sind es gerade diese Faktoren, die letztendlich den Erfolg von Strategien zur Erhöhung der Speicherkapazität von Böden ausmachen. Aufgrund dieser Erkenntnis ist es notwendig, weitere wissenschaftliche Forschungen über die Dynamik organischen Kohlenstoffs in Böden durchzuführen, um unser Verständnis zu verbessern und das Potenzial von Böden als Senken für Kohlenstoff besser zu beschreiben.

Theoretischer Hintergrund

Es gibt eine wachsende Anzahl von Studien, die Belege für die Bedeutung von Bodengefüge und mineralogischer Faktoren bei der Stabilisierung organischer Substanzen in Böden vorlegen. Diese Faktoren mögen letztendlich die Kapazität von Böden beeinflussen, Kohlenstoff zu speichern. Die Bedeutung von Sorptionsprozessen speziell auf tonmineralischen Oberflächen bei der Fixierung organischen Materials in Böden hat hierbei eine spezielle Beachtung gefunden. Obwohl die Frage, auf welche Weise Adsorption zur Stabilisierung organischer Substanz in Böden führt, nach wie vor nicht beantwortet ist, haben Studien gezeigt, dass eine positive statistische Beziehung zwischen der spezifischen Oberfläche von Sedimenten und Bodenpartikeln einerseits und der Konzentration organischen Kohlenstoffs andererseits besteht. So hat insbesondere Mayer (1994a) eine enge Beziehung zwischen dem Gehalt von organischem Kohlenstoff und der spezifischen Oberfläche von marinen Sedimenten festgestellt. Er bezeichnet diese Beziehung in seiner Arbeit als das „monolayer equivalent“. Seine Erkenntnisse werden durch die Arbeit anderer Wissenschaftler wie etwa Keil et al. (1994a) gestützt. Der Zusammenhang zwischen spezifischer Oberfläche und organischem Kohlenstoffgehalt ist für Böden nur zum Teil belegt worden (Mayer 1994b; Sagger et al. 1996). Bei der Hälfte der von Mayer (1994b) untersuchten Böden korrelierte die Konzentrationen des organischen Kohlenstoffs nicht mit der spezifischen Oberfläche. Auch bei den Bodenanalysen von Kaiser und Guggenberger (2000) konnte diese Beziehung nicht bestätigt werden.

Einigen Tonmineralen (speziell Smectiten) werden aufgrund ihrer großen spezifischen Oberfläche eine höhere Aufnahmefähigkeit für organische Substanz zugesprochen. Die große spezifische Oberfläche ist vor allem in den Zwischenschichten dieser quellfähigen Minerale zu finden. Diese Annahme wird gestützt durch eine Vielzahl von Laborstudien, die gezeigt haben, dass solche Tonminerale in der Lage sind, organische Substanz in großen Mengen einzulagern (Greenland 1965a; Weiss 1969; Mortland 1970). Ob dies allerdings auch unter den in der Natur vorherrschenden Bedingungen geschieht, ist nicht klar. Bisher wurde nur in drei Studien gezeigt, dass die Einlagerung von organischem Material in den Zwischenschichten von Böden mit hohem Anteil von Smectiten und organischer Substanz mit einem pH-Wert unter 5 erfolgt, da dann die negative Ladung der organischen Polymere unterdrückt wird (Theng et al. 1986; Schnitzer et al. 1988; Schulten et al. 1996).

Wenn man die Unterschiede verschiedener Tonminerale bei der Fixierung organischer Substanz in Böden unberücksichtigt lässt, so scheint die Tonfraktion generell einen stabilisierenden Einfluss auf den Gehalt von organischem Material zu haben. Einerseits wurde für Böden in gemäßigten Breiten gezeigt, dass die Konzentration organischen Kohlenstoffs mit zunehmender Korngröße sinkt (Turchenek und Oades 1979; Anderson et al. 1981; Tiessen und Stewart 1983; Balesdent et al. 1988; Cambardella und Elliot 1993; Buyanovsky et al. 1994). Die größten Mengen organischer Substanz in Böden wurden in diesen Studien in den Schluff- und speziell den Tonfraktionen der Böden gefunden. Andererseits steigt offensichtlich die Konzentration organischen Kohlenstoffs in einem Boden auch mit dem Tongehalt an. Dies deutet darauf hin, dass Tonpartikel ebenfalls eine stabilisierende Wirkung haben (Christensen 1992).

Bisherige Studien haben sich vor allem auf die Rolle von Tonmineralen (Phyllosilicaten) bei der Fixierung organischer Substanz in Böden konzentriert. Dies kann dann als problematisch angesehen werden, wenn Oxide, die in solchen Studien ausgeschlossen wurden, in den Böden quantitativ von größerer Bedeutung sind als Tonminerale. Boudot et al. (1988) haben zum Bespiel festgestellt, dass der Abbau von organischem Kohlenstoff und Stickstoff in acht verschieden Böden stark reduziert war, wenn amorphe Eisen- und Aluminiumoxide vorhanden waren. Labor- und Feldstudien über die Interaktion von Oxiden mit organischer

Substanz waren bisher meist sehr eng fokussiert auf diese Minerale und haben potenzielle Interaktionen mit Tonmineralen unter realen Bedienungen weitgehend ignoriert. Oxide verbinden sich jedoch leicht mit Tonmineralen (Goldberg und Glaubig 1987; Goldberg 1989; Schwertmann und Taylor 1989) und formen unter Umständen Komplexe, die einen signifikanten Einfluss auf die Kapazität von Böden zur Ablagerung von Kohlenstoff haben können.

Angesichts der vorhandenen Wissenslücken und widersprüchlichen empirischen Ergebnisse bezüglich der Mechanismen bei der Fixierung organischer Substanz in Böden ist es notwendig zu untersuchen, welche Rolle verschiedene geochemische Faktoren bei der Ablagerung organischen Kohlenstoffs in Böden spielen. Es ist deshalb notwendig, mehr *in situ*-Untersuchungen durchzuführen, denn viele Studien über Oxide und die Einlagerung organischen Materials in quellfähige Tonminerale fanden bisher unter Laborbedingungen mit „reinen“ Partikeln statt. Das Verhalten solche Partikel im Versuch mag jedoch nicht repräsentativ für das Verhalten von Mineralen unter realen Bedingungen sein, deren Aufnahmefähigkeit aufgrund der Verbindung mit anderen Mineralen und organischen Substanzen sehr unterschiedlich sein kann. Zudem konzentrierten sich die meisten Studien auf den organischen Kohlenstoffgehalt in Oberböden und vernachlässigten somit die Dynamik organischen Kohlenstoffs in Unterböden. Dies ist problematisch, da gezeigt wurde, dass Unterböden einen substanziellen Anteil der organischen Kohlenstoff-Ablagerungen in Böden enthalten (siehe Kaiser et al. 2002a). Da Unterböden sich besser dazu eignen, Aussagen über die längerfristige Kapazität von Böden zur Speicherung von Kohlenstoff zu treffen, ist es von großer Bedeutung, diese ebenfalls zu untersuchen.

Zweck und Ziel der Untersuchung

Vor dem Hintergrund der oben angesprochenen Zusammenhänge besteht der Zweck der vorliegenden Studie darin, die Konzentration von organischem Kohlenstoff und Stickstoff für unterschiedliche Bodentypen und mineralogische Zusammensetzungen zu untersuchen und die Wirkung der Tonmineralogie, der spezifischen Oberfläche und der Oxidkonzentration auf die Kohlenstoff- und Stickstoffkonzentration zu analysieren. Ziel der Studie ist es, einen Beitrag zu liefern, um die Mechanismen der Fixierung organischer Substanz in Böden besser zu verstehen und das vorhandene Wissen hierüber zu erweitern. Dies kann uns dabei helfen aufzuklären, welche Kapazität Böden zur Fixierung von organischem Kohlenstoff in Abhängigkeit von ihrem Gefüge und ihrer mineralogischen Zusammensetzung haben.

Untersuchte Bodenprofile und durchgeführte Analysen

Um den Zweck dieser Studie zu erfüllen, wurden fünf verschiede Bodenprofile aus Hessen mit unterschiedlicher Mineralogie untersucht. Diese sind in der folgenden Tabelle dargestellt.

Tabelle Z.1: Standorte und Eigenschaften der untersuchten hessischen Böden

Standort	**Bodentyp**	**Ausgangssubstrat**	**Tonmineralogie**
Profil 1: Münden 1, Rheinhardswald	schwach pseudovergleyte podsolige Braunerde	Lösslehm und Bundsandsteinschutt	Vermiculit, Chlorit, Illit, Illit-Smectit-Wechsellagerungsminerale, Kaolinit
Profil 2: Münden 2, Rheinhardswald	Pseudogley-Parabraunerde	Lösslehm	Vermiculit, Chlorit, Illit, Illit-Smectit-Wechsellagerungsminerale, Kaolinit
Profil 3: Königstein, Taunus	podsolige Braunderde	Lösslehm und Tonschieferschutt	Vermiculit, Chlorit, Illit, Illit-Smectit-Wechsellagerungsminerale, Kaolinit
Profil 4: Geinsheim, Oberrhein	Kolluvisol über Pelosol über Gley-Kalktschernosem	Kolluvisol aus umgelagerten Auensedimenten, Pelosol aus schwarzem Auentonen, Gley-Kalktschernosem aus Auenschluffen über Auensanden	Smectit, Illit, Illit-Smectit-Wechsellagerungsminerale, Chlorit, Kaolinit
Profil 5: Frankfurter Stadtwald, Frankfurt am Main*	Gley	Auenton über Auensand	Smectit, Illit, Illit-Smectit-Wechsellagerungsminerale, Chlorit, Kaolinit

*Das fünfte Profil des Frankfurter Stadtwalds wurde bereits vor dieser Untersuchung als Teil eines Projekts von Jörg Disselkamp-Tietze analysiert (Disselkamp-Tietze 2000).

Zusätzlich zu einer Reihe grundlegender Parameter wie zum Beispiel pH, Carbonat-Gehalt und Korngrößenverteilung wurden die folgenden Analysen durchgeführt, um die

Auswirkungen verschiedener physikalischer und geochemischer Faktoren auf den Gehalt organischer Substanz in den untersuchten Böden festzustellen:

- Tonmineralogie
- organische Kohlenstoff- und Stickstoff-Konzentrationen
- %-Kationensättigung
- spezifische Oberfläche
- dithionit- und oxalatlösliche Fe, Mn und Al.

Anhand dieser Parameter wurden weiterführende statistische Analysen unter Verwendung der Statistiksoftware SPSS für Windows durchgeführt, um mögliche statistische Beziehungen und Zusammenhänge aufzudecken, die für die Stabilisierung von organischem Kohlenstoff in den betrachteten Böden verantwortlich sind.

Untersuchungsergebnisse

Im Unterschied zu den oftmals selektiven Ergebnissen in der Literatur zeigt die vorliegende Studie, dass der Tonanteil und die Tonmineralogie der untersuchten Böden nur einen begrenzten Einfluss auf die Stabilisierung organischer Substanz haben. Diese Schlussfolgerung wird durch zahlreiche Beobachtungen gestützt:

- Nur für die beiden Profile Königstein und Geinsheim gibt es eine signifikante positive Korrelation zwischen dem Tonanteil und dem organischen Kohlenstoffgehalt in den Gesamtproben. Im Fall des Profils Königstein ist allerdings nicht klar, ob diese Beziehung tatsächlich besteht, da sowohl Tonanteil und als auch Kohlenstoffgehalt mit zunehmender Tiefe abnehmen. Hier mag der Tonanteil des Bodens nicht unbedingt eine kausale Erklärung für die Variation des organischen Kohlenstoffgehalts liefern.
- Die Profile Geinsheim und Frankfurter Stadtwald weisen keine großen Konzentrationen von organischem Kohlenstoff und Stickstoff auf, obwohl man dies angesichts des hohen Tongehalts hätte erwarten können. In beiden Profilen gibt es große Anteile Smectite, von denen angenommen wird, dass sie aufgrund ihrer größeren spezifischen Oberfläche eine größere Kapazität zur Fixierung organischer Substanz besitzen.

- Insgesamt gibt es nur eine begrenzte Anzahl von Tonmineralen, die signifikante positive Korrelationen mit der Konzentration organischen Kohlenstoffs und Stickstoffs in den untersuchten Profilen aufweisen. Während Smectite keine signifikante Korrelation mit der organischen Substanz im Geinsheim-Profil aufweisen, konnte für Kaolonit im Unterschied dazu eine signifikante positive Beziehung mit dem organischen Kohlenstoff- und Stickstoffgehalt in den Proben beobachtet werden.
- Austauschbare Kationen, die eine hohe Affinität mit organischer Substanz in den untersuchten Bodenprofilen zu haben scheinen, weisen nur mit wenigen Tonmineralen eine signifikante Korrelation auf. Dies kann als Anzeichen dafür gewertet werden, dass Tonminerale nur indirekt an der Stabilisierung von organischem Material in Böden beteiligt sind.

Zudem zeigt die vorliegende Studie, dass die Beziehung zwischen spezifischer Oberfläche und der Konzentration organischen Kohlenstoffs, wie sie von Mayer (1994a) postuliert wird, nicht auf alle Böden anwendbar ist. Die für die Schluff- und Tonfraktionen ermitteln Konzentrationen von organischem Kohlenstoff überwiegend nicht in den Bereich des erwarteten „monolayer equivalent“-Intervalls zwischen 0,6 und 1,5 mg C m^{-2} fallen. Für die Profile Münden 1 und 2 sowie Königstein wurden in den A-Horizonten größere Konzentrationen festgestellt, während die Werte für die B- und C-Horizonte für alle Profile unterhalb des „monolayer equivalent“-Intervalls lagen. Allerdings sind die Ergebnisse auch in der Literatur bezüglich der Anwendung des „monolayer equivalent“-Konzepts auf Böden widersprüchlich. So haben Mayer (1994b) und Mayer und Xing (2001) analog zu den hier erzielten Ergebnissen gezeigt, dass eine große Zahl von Böden Konzentrationen von organischem Kohlenstoff aufweisen, die entweder oberhalb oder unterhalb des „monolayer equivalent“-Intervalls liegen. Diese Ergebnisse deuten darauf hin, dass die Anwendung des Konzepts auf Böden möglicherweise unangemessen ist.

Die Tatsache, dass die meisten Profile Konzentrationen von organischem Kohlenstoff aufweisen, die nicht dem „monolayer equivalent“ von Mayer (1994a) entsprechen, bedeutet jedoch nicht, dass Sorptionsprozesse und die spezifische Oberfläche von Böden bei der Stabilisierung von organischer Substanz in Böden gänzlich unbedeutend sind. Es ist nicht zu erwarten, dass organisches Material auf der Oberfläche von Mineralen gleich verteilt ist. Es ist vielmehr wahrscheinlich, dass organische Substanz in Form kleiner Partikel und als mehrfache Schichten („multilayer coatings“) sowohl auf als auch zwischen Mineralen lokalisiert ist. Mayer selbst warnt mittlerweile ebenfalls vor der leichtfertigen Verwendung des Begriffs des „monolayer equivalent“ (siehe Mayer 1999; Mayer und Xing 2001), da dieser fehlleitend sein kann. Bei zwei der fünf untersuchten Profile (Königstein und Geinsheim) zeigte sich eine signifikant positive Korrelation zwischen der spezifischen Oberfläche der Böden und der Konzentration von organischem Kohlenstoff. Im Fall des Profils Königstein ergibt sich diese Beziehung nur, wenn der Oberboden nicht in die Analyse einbezogen wird. Aufgrund der großen Mengen organischer Einträge im Fall des Königstein-Profils kombiniert mit einem geringen pH-Wert ist es wahrscheinlich, dass jede Art von Beziehung zwischen spezifischer Oberfläche und organischer Substanz in diesem Profil verdeckt wird. Die größten Konzentrationen von organischem Kohlenstoff sind in der vorliegenden Studie generell in den kleinsten Fraktionen zu finden (Feinschluff und Ton). Das Nicht-Vorhandensein einer starken signifikanten Beziehung zwischen Tonanteil, Tonmineralzusammensetzung, spezifischer Oberfläche und der Konzentration von organischem Kohlenstoff bei den meisten untersuchten Profilen deutet jedoch darauf hin, dass Sorptionsprozesse nicht so bedeutend sind, wie in der Literatur oftmals angenommen wird. Es muss also noch andere Faktoren geben, die ebenso wichtig oder sogar noch wichtiger für die Stabilisierung von organischem Material in diesen Böden sind. Hierzu mag etwa die Mikroporosität der Boden gehören, die in großem Maß durch das Vorhandensein sowohl von Tonmineralen als auch von Oxiden verstärkt wird.

In diesem Kontext belegt die vorliegende Untersuchung, dass Oxide, vor allem die schlecht kristallisierten, eine große Rolle bei der Fixierung von organischer Substanz in den untersuchten Böden spielen. Amorphe Eisen- und Aluminiumoxide sind besonders bedeutend in den Profilen Königstein und Geinsheim. Im Fall des Profils Münden 1 zeigt sich ebenfalls eine starke Korrelation zwischen der Konzentration organischen Kohlenstoffs und dem Anteil oxalatlöslichen Eisens und Aluminiums, wenn man den A-Horizont nicht berücksichtigt. Im Fall des Profils Geinsheim spielen schlecht kristallisierte Eisenoxide eine größere Rolle bei der Stabilisierung organischen Materials als Aluminiumoxide. Dies steht im Widerspruch zu den Ergebnissen von Boudot et al. (1988), die gezeigt haben, dass organischer Kohlenstoff und Stickstoff eine stärkere Affinität zu oxalatlöslichem Aluminium als zu oxalatlöslichem Eisen haben. Die Resultate dieser Studie entsprechen den Ergebnissen des Profils Münden 2, bei dem amorphe Aluminiumoxide für die Stabilisierung organischer Substanz ebenfalls bedeutender sind als Eisenoxide. Im Fall des Profils Frankfurter Stadtwald korrelieren oxalatlösliches Eisen und Aluminium stark mit den Konzentrationen organischen Kohlenstoffs und Stickstoffs.

Allerdings bedeutet dies nicht, dass Tonminerale für die Fixierung organischen Materials unerheblich sind. Die Ergebnisse für die untersuchten Böden deuten darauf hin, dass sich Komplexe aus Ton, Oxiden und organischer Substanz bilden, die auch zu einer Stabilisierung organischen Materials führen. Dies kann aus einer Anzahl statistisch signifikanter Beziehungen zwischen Tonmineralen und dithionit- und oxalatlöslichem Eisen und Aluminium abgeleitet werden. Solche Komplexe scheinen im Fall der Königstein- und Geinsheim-Profile vorhanden zu sein. Im Profil Geinsheim scheint Kaolinit mit Oxiden (insbesondere mit Eisenoxiden) zu interagieren und Aggregate zu bilden, die organische Substanz stabilisieren. Es mag allerdings auch sein, dass Kaolinit organisches Material direkt bindet. Ähnlich wie Oxide besitzt Kaolinit reaktive Flächen mit zugänglichen Hydroxyl-Gruppen mit variabler Ladung (Theng 1974; Tan 1998). Im Fall der Profile Münden 2 und Frankfurter Stadtwald scheinen Komplexe mit Ton, Oxiden und organischem Material allerdings nicht signifikant oder nicht existent zu sein.

Schlussfolgerungen und Ausblick

Die Präsenz von amorphen Eisen- und Aluminiumoxiden scheint der wichtigste Einflussfaktor für die Fixierung von organischem Material in den untersuchten Böden zu sein. Die größeren Konzentrationen von organischem Kohlenstoff in den kleinsten Fraktionen (Feinschluff und Ton) in allen Profilen sind vor allem darauf zurückzuführen, dass Oxide genau in diesen Fraktionen aufzufinden sind. Zusätzlich scheinen Tonminerale eine sekundäre Bedeutung bei der Stabilisierung organischer Substanz zu haben. Dabei sollte man die Signifikanz von Tonmineralen jedoch nicht unterbewerten. Sie sind speziell im Fall der Profile Königstein und Geinsheim von Bedeutung. Das Fehlen einer signifikanten Beziehung zwischen Tongehalt und spezifischer Oberfläche auf der einen Seite und organischer Substanz auf der anderen Seite deutet daraufhin, dass es in den anderen Profilen außer der Adsorption von organischem Material noch weitere Mechanismen geben muss, die eine wichtige Rolle spielen. Anhand der Ergebnisse dieser Studie in Verbindung mit Beobachtungen in der Literatur kann folgendes Modell des Prozesses der Stabilisierung organischer Substanz in Böden postuliert werden:

- In den meisten Bodenprofilen bewirken Oxide starke Adsorptionsprozesse die speziell dort, wo die Bodenbedinungen sauer sind, zu einer Fixierung organischen Materials führen.
- Tonminerale unterstützen die Stabilisierung organischer Substanz, indem sie mit Oxiden Komplexe bilden, die die Basis für Aggregate darstellen und die Mikroporosität der Böden erhöhen.

Ungeachtet der Mechanismen, die bei der Stabilisierung organischen Kohlenstoffs beteiligt sind, bleibt jedoch die Frage offen, ob organisches Material über einen längeren Zeitraum in Böden gespeichert werden kann und ob diese Böden deshalb als Senke für atmosphärischen Kohlenstoff dienen können. Die Abnahme in der Konzentration organischen Kohlenstoffs in den Gesamtproben und den Tonfraktionen mit zunehmender Tiefe deutet darauf hin, dass organische Substanz nicht permanent stabilisiert, sondern mit der Zeit degradiert wird. Im Fall des Profils Geinsheim scheint organisches Material zumindest zu einem gewissen Grad gespeichert zu werden, was sich hier anhand der relativ stabilen Konzentration von organischem Kohlenstoff in Abhängigkeit von der Tiefe darstellt. Es bleibt jedoch offen, ob dies die Folge eines schützenden Mechanismus ist oder lediglich eine Auswirkung des Transports von organischer Substanz nach unten durch Quell- und Schrumpfungsprozesse der Smectite.

Insgesamt deuten die Ergebnisse darauf hin, dass Böden keine geeignete Senke für die langfristige Speicherung von organischem Kohlenstoff sind. Für die meisten Böden kann man erwarten, dass die Menge organischen Materials, das gespeichert werden kann, begrenzt ist. Falls der organische Gehalt eines Bodens größtenteils durch Adsorptionsprozesse kontrolliert wird, ist anzunehmen, dass die Größe der verfügbaren spezifischen Oberfläche ein limitierender Faktor ist. Hassink (1997) hat in einer Studie den Kohlenstoff- und Stickstoffgehalt von Schluff- und Tonfraktionen einer Anzahl nicht-kultivierter Böden in gemäßigten Breiten und tropischen Regionen untersucht und festgestellt, dass die Konzentrationen dabei weitgehend dieselben waren. Dies deutet darauf hin, dass das Maximum an Kohlenstoff- und Stickstoffkonzentration, das bei diesen feinen Fraktionen möglich ist, bereits erreicht war. Zudem schien die Konzentration nicht durch den Tonmineraltyp beeinflusst zu werden. Obwohl Mechanismen wie die Adsorption von organischer Substanz an Oxide die Stabilisierung organischen Materials unterstützen, scheinen diese nicht stark genug zu sein, um eine permanente Speicherung von organischem Kohlenstoff zu bewirken. Dies wird durch die Tatsache belegt, dass die Konzentration von organischem Kohlenstoff in den untersuchten Profilen mit zunehmender Tiefe abnimmt.

Man könnte sogar argumentieren, dass viele Böden weltweit in Zukunft wichtige Quellen von CO_2 werden. Feuchtgebiete, die historische Senken für Kohlenstoff sind, haben sich schon heute in vielen Teilen der Welt zu Quellen von CO_2 gewandelt (Eswaran et al. 1995). In dem Maß, in dem sie für Bautätigkeit und landwirtschaftliche Nutzungen trocken gelegt werden, geht ein großer Teil des Kohlenstoffs in Form von CO_2 verloren. Weitere Böden vor allem in nördlichen Breiten, die in der Vergangenheit als Senken für Kohlenstoff dienten, können in Zukunft ebenfalls zu Quellen für CO_2 werden, wenn sich das Klima weiterhin ändert und Temperaturen durch die globale Erwärmung ansteigen (Kohlmaier 1989; Goulden et al. 1998). So wird erwartet, dass Permafrost in vielen Gebieten zurückgehen wird, falls die globalen Temperaturen bis zum Jahr 2100 um rund 2 °C ansteigen sollen. Dies könnte in der Folge dazu führen, das große Mengen CO_2 in die Atmosphäre freigesetzt werden.

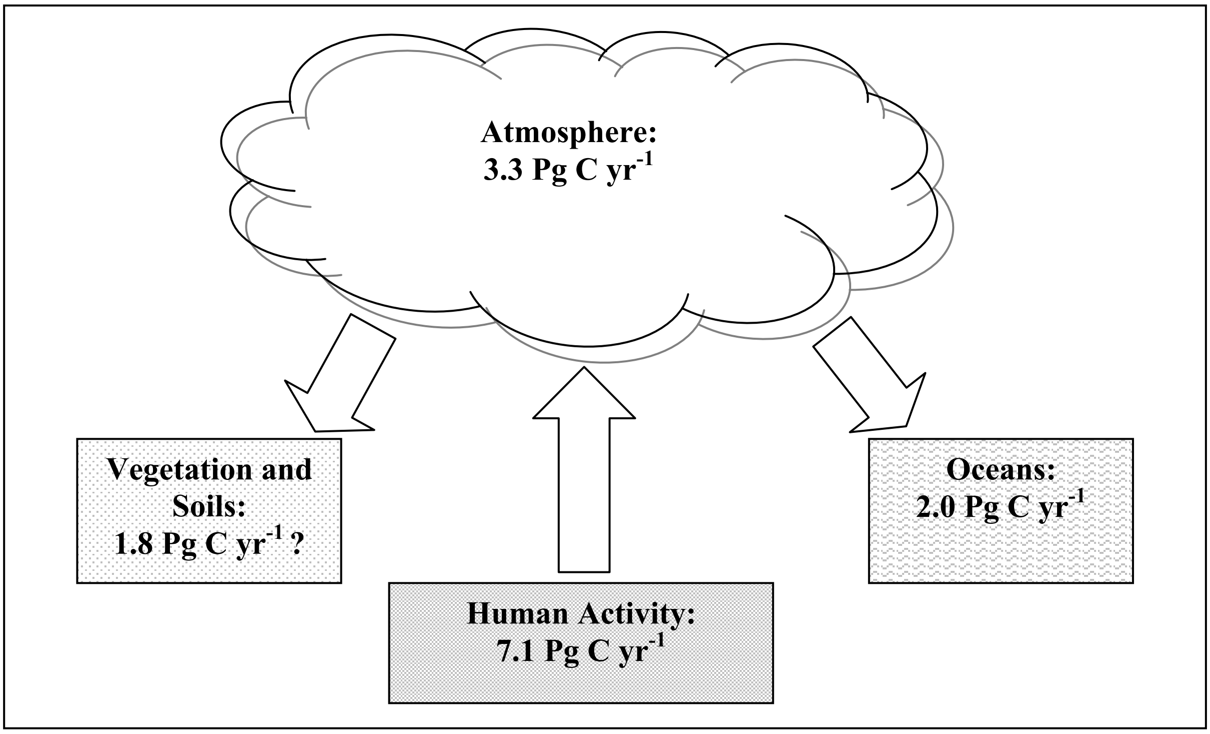
Versuche, durch Eingriffe die Kohlenstoff-Speicherkapazität von Böden zu erhöhen, mögen zwar helfen, klimatische Probleme, die mit erhöhten Konzentrationen von atmosphärischem CO_2 verbunden sind, zu vermindern. Diese Kapazität wird jedoch sehr begrenzt und eher kurzfristiger Natur sein. Vorhergesagte Anstiege in globalen Temperaturen mögen Bemühungen entgegen wirken, die Kohlenstoffaufnahme von Böden zu erhöhen. Langfristige Lösungen erfordern, dass die Treibhausgas-Emissionen dauerhaft reduziert werden. Dies setzt eine globale Partizipation und die Entwicklung kreativer Lösungen voraus, um Entwicklungsländer dabei zu unterstützen, ihre voraussichtlichen CO_2-Emissionen auf ein möglichst geringes Maß zu reduzieren.

1. Introduction

1.1 The Global Carbon Cycle and the Importance of Soils

As the climatic effects of greenhouse gas emissions become more apparent, there has been increasingly greater interest in recent years in identifying and utilizing potential carbon sinks to reduce atmospheric levels of CO_2. Of the total 7.1 Pg C emitted through human activity every year, the atmosphere is estimated to adsorb 3.3 Pg C yr^{-1}, while the ocean takes up about 2.0 Pg yr^{-1} (Houghton et al. 1998). This leaves an approximate 1.8 Pg of C yr^{-1} which is unaccounted for in models of the global carbon cycle (see Figure 1.1 for an overview of the global carbon cycle). It is generally accepted that terrestrial sinks, notably trees and soils, are responsible for this "missing" sink (Tans et al. 1990; Ciais et al. 1995; Keeling et al. 1996; Fan et al. 1998). Factors that have been identified for an enhanced uptake of atmospheric carbon include forest growth and regeneration, possibly stimulated by CO_2 and nitrogen enrichment (Norby et al. 1992; Luxmoore et al. 1993; Curtis 1996). As such, forest management strategies are viewed by many countries as a major way to meet CO_2 reductions, as agreed to under the Kyoto Protocol to the UN Convention on Climate Change.

Figure 1.1: The Global Carbon Cycle*



*Estimates taken from Houghton et al. (1998)

Soils are an important pool for carbon and play a critical role in the global carbon cycle. Most of the approximate 2000 Pg of carbon which is stored in terrestrial systems is contained in soils. Specifically, estimates for global soils range from about 1400 Pg C (Post et al. 1982) to almost 1600 Pg C (Eswaran et al. 1993). About half of the 120 Pg C yr^{-1} which is fixed by plants from the atmosphere eventually makes its way into soils in the form of above- and belowground litter and root exudates where it is respired by microorganisms, leached as dissolved organic matter or stabilized and preserved in organomineral complexes. Although clearly a significant *pool* of carbon, the importance of soils as a potential long term *sink* for atmospheric carbon is, however, not clear. Strategies which help to increase the carbon sequestration of soils to mitigate atmospheric carbon have received increasingly more attention in recent years (e.g. Batjes 1999). This has, in part, been stimulated by Article 3.4 of the Kyoto Protocol, which suggests that "*sources and removals by sinks in the agricultural soils and the land-use change and forestry categories*" be considered in the future, opening up the way for countries to use soils to meet their emission reductions.

Modelling and experimental results do suggest that soils have a significant potential to sequester carbon. Dumanski et al. (1998) suggest, for instance, that agricultural lands in Canada could sequester 1.8 Tg C yr^{-1} over the next 50 years given the right cropping systems and land management techniques. Agricultural soils in the former Soviet Union have been estimated to have an even greater potential to sequester carbon, with as much as 340 Tg C yr^{-1} (Kolchungina et al. 1995). Batjes (1999) believes that global agricultural soils could sequester about 14±7 Pg C over the next 25 years. Estimates of the Intergovernmental Panel on Climate Change (IPCC) in its Second Assessment Report for croplands are even higher, with a calculated sequestration potential of between 40 and 80 Pg of carbon over the next 50 to 100 years (Cole et al. 1996).

Although soils have the potential to play an important role in alleviating atmospheric CO_2 levels, the use of results of large-scale modelling efforts and local-scale studies on the effects of landscape change and management on soil carbon turnover as a basis for developing strategies for CO_2 mitigation are potentially problematic. Specifically, knowledge gaps regarding the biogeochemical mechanisms involved in the sequestration of carbon in soils, particularly over the long term, could hinder the implementation of such strategies. The outcome could, in fact, be not only unproductive but damaging. As a consequence of different biogeochemical factors such as mineralogical composition, not all soils have an equal potential to take up and store carbon. The impact of soil type and mineralogy on the capacity of soils to sequester atmospheric carbon has generally, however, not received enough attention in the formulation of strategies to reduce atmospheric CO_2 levels. Although there has been great progress made in recent years regarding our understanding of carbon cycling in soils, some open questions remain regarding the specific mechanisms responsible for organic carbon stabilization and sequestration. As Sollins et al. (1996) point out "most of the stabilization mechanisms are not well understood, their rates cannot be measured in the soil, and there is no way to construct budgets of the carbon and nutrient fluxes that result from them. Indeed, we lack even the most basic information on the factors controlling them." Ultimately, knowledge regarding these factors will determine the success of strategies to increase the storage capacity of soils. In light of this, there is a need for more research regarding organic carbon dynamics in soils to improve our understanding and help us better characterize the potential of soils to serve as a carbon sink.

1.2 Mechanisms of Soil Organic Carbon Sequestration

There is a growing body of literature which provides evidence for the importance of textural and mineralogical factors in soil organic matter stabilization, factors which may ultimately influence a soil's capacity to store carbon. The significance of sorptive processes, particularly on clay mineral surfaces, in the preservation of organic materials has especially received a great deal of attention. Although the question of how adsorption leads to the protection of organic matter remains open, studies have demonstrated a positive relationship between the specific surface area (SSA) of sediments and soil particles and organic carbon contents. Notably, Mayer (1994a) has demonstrated the existence of a strong relationship between organic matter concentrations and mineral surface area, a relationship which he refers to as the "monolayer equivalent" in his work on aluminosilicate sediments on continental shelves. Keil and his colleagues (1994a) showed that this observed relationship between organic matter and surface area seems to be due to some protective mechanism and is not simply the result of the presence of recalcitrant forms of organic carbon. Specifically, decomposition of organic matter occurred at a rate of five orders of magnitude faster upon desorption from minerals, indicating the labile nature of the organic compounds associated with mineral surfaces. There is conflicting evidence, however, regarding this relationship between SSA and organic carbon content. Kaiser and Guggenberger (2000), for instance, in their analysis of the behaviour of dissolved organic matter in soils, demonstrated that there was no significant relationship between organic carbon concentrations and SSA. In an investigation of terrestrial soils, Mayer (1994b) himself found that the organic carbon concentrations of about half of the soils did not correlate with SSA.

Certain clay minerals, notably smectites, are predicted to have a greater sorptive capacity for organic materials given their large SSA, most of which is contained in the interlayer of these expanding minerals. This is supported by a large number of laboratory studies which have demonstrated the readiness of such clays to intercalate organic compounds (Greenland 1965a; Weiss 1969; Mortland 1970). Whether this actually occurs under natural conditions, however, is not clear. Interlayer complex formation has only been shown to occur in smectite- and organic-rich soils with a pH below 5, when the negative charge of polymers is suppressed (Theng et al. 1986; Schnitzer et al. 1988). It is, thus, not clear whether the intercalation of organic compounds by such minerals plays a significant role in the natural environment.

Ignoring potential differences in the capacity of individual clay minerals to stabilize organic matter, it appears as if the clay particle size fraction generally has a protective effect on organic materials in soils. First, it has been demonstrated that, at least for temperate soils, organic carbon concentrations increase with decreases in particle size (see Turchenek and Oades 1979; Anderson et al. 1981; Tiessen and Stewart 1983; Balesdent et al. 1988; Cambardella and Elliot 1993; Buyanovsky et al. 1994). Most soil organic matter has been found to be associated with the silt- and, especially, the clay particle size fractions. Greenland (1965a) has suggested that as much as 90% of organic matter is intimately associated with the clay mineral fraction. Further, it appears that the organic carbon concentration of a soil also increases with clay content, which also suggests that clay size particles have a protective effect (Christensen 1992). In contrast to these studies, however, some evidence indicates that clay content may not be an important protective factor for some soils, as reflected by the absence of a correlation between clay content and soil organic carbon concentrations in several studies (e.g. Saggar et al. 1996; Mayer and Xing 2001).

Although the focus of past investigations has been on the role of clay minerals (i.e. phyllosilicates) in the stabilization of organic matter, oxides may be partially responsible for observed relationships between organic carbon contents and the clay particle size fraction and SSA. Oxides, which also typically have a large SSA and fall within the particle size range defined for clays (i.e. <2 µm in diameter), have been demonstrated to have a large protective capacity. Boudot et al. (1988) found, for instance, that organic carbon and nitrogen mineralization rates in eight different soils were strongly reduced in the presence of amorphous iron and aluminium oxides. In an investigation of volcanic soils, Torn et al. (1997) found that non-crystalline minerals, including the ferrihydrite, accounted for >40% of the variation observed in organic carbon contents across all mineral horizons and soil orders. Laboratory studies on the interaction of oxides and organic material, of which dissolved organic matter has typically been the focus, have usually neglected potential interactions with clay minerals in the natural environment. Oxides readily bind to both clay minerals and organic material though (Goldberg and Glaubig 1987; Goldberg 1989; Schwertmann and Taylor 1989), forming potential complexes which may be a significant factor in the capacity of a soil to sequester carbon.

In light of the above, it would appear that sorptive processes are important in the stabilization of organic matter in soils. The following questions remain, however, open:

- Are adsorptive processes significant in the protection of organic matter in all soils? To what extent may other factors such as soil porosity and aggregation play a role in the protection of organic matter?
- Can established relationships between SSA and organic carbon content be applied to most soils?
- Are certain clay minerals more important than others in sequestering organic matter? Do organic materials intercalate into the interlayers of expanding minerals under natural conditions?
- What is the role of oxides and how do they interact with clay minerals in stabilizing soil organic matter?
- How does an association with mineral surfaces lead to the protection of organic matter? Is organic matter protected over the long term?

There is a need to investigate the above open questions to sufficiently judge what soil textural or mineralogical factors play a role in the preservation of organic carbon in soils. In particular, there is a need to conduct more investigations *in situ* or on soils in the natural environment, as much investigative work, especially on oxides and the intercalation of organic compounds of swelling clay minerals, has been done in the lab on “clean” particles. The behaviour of such particles may not be reflective of minerals *in situ,* whose sorptive capacities may be very different given mineral and organic coatings. Further, most studies of the past have focused on organic carbon in the topsoil, to the neglect of organic carbon dynamics in the subsoil. This is unfortunate as subsoils have been shown to contain a substantial portion of the total organic carbon content of a soil (see Kaiser et al. 2002a). As subsoils would be better reflective of the long term capacity of soils to store carbon, there is also a need for their investigation. Finally, there have been few studies which have systematically examined the breadth of known and suspected structural, chemical and mineralogical factors, including their interaction, in stabilizing organic material in the soils investigated. As Baldock and Skjemstad (2001) point out, however, “Quantifying the protective capacity of a soil requires a careful consideration of all mechanisms of protection”.

1.3 Study Purpose and Objectives

Given the above issues, the purpose of this study was to examine the importance of sorptive mechanisms on OC stabilization. The objectives were: (1) to determine the SSA, clay mineralogy and dithionite- and oxalate-extractable Fe, Mn and Al concentrations of several soils, and (2) to analyse how these parameters are related to OC concentrations. It should be noted that the term “clay mineral” will only refer to members of the phyllosilicates, a class of the silicate mineral group characterized by the sharing of three of the four oxygens in each tetrahedron with other tetrahedra to form sheet-like structures (see Olson et al. 2000). Although all of the above questions cannot be answered within the realm of this study, the goal is to contribute to an increased understanding and expansion of the body of knowledge regarding the mechanisms of organic matter preservation in soils. This, in turn, will help us elucidate the capacity of soils to sequester atmospheric carbon given their textural and mineralogical composition.

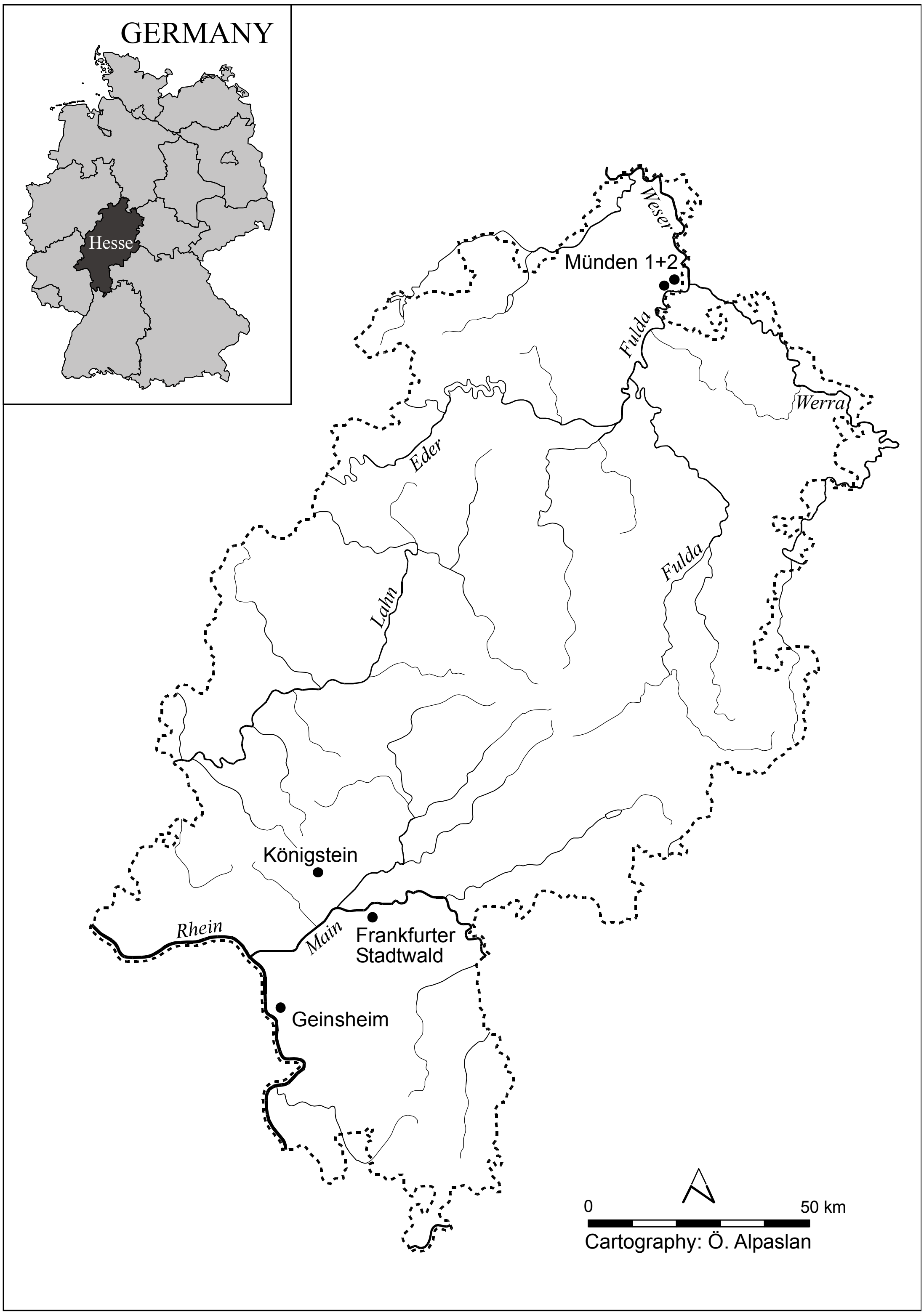
This paper will be structured as follows. Chapter 2 will describe the soil profiles sampled and their characteristics. Chapter 3 will then discuss the sampling and analytical methods used to investigate the various physico-chemical and mineralogical parameters of study interest. The statistical analyses conducted will also be briefly presented. This will then be followed by a presentation of the laboratory results of the various soil parameters investigated in Chapter 4. Chapter 5 will discuss the results of statistical analyses undertaken. The results and their implications will then be discussed at length in Chapter 6. Comparisons to other studies will also be made and theoretical contributions to the topic presented. This will then conclude with a discussion of possible mechanisms which may play a role in the stabilization of organic matter in the soils under investigation in Chapter 7. The potential of soils to sequester carbon in the larger context of CO_2 emissions and the global carbon cycle in light of the study results will be briefly addressed in Chapter 8.

2. Soil Profiles Investigated: Location and Description

Two primary criteria were used to select sites for investigation. First, soils were chosen based on their representativeness; that is, an emphasis was placed on choosing soils common to temperate areas to allow generalizations to be made regarding the wider implications of study results. Second, variability between sites in terms of their mineralogical composition, particularly clay mineralogy, was a primary factor of consideration. In particular, an attempt was made to select at least two soil profiles which contain smectites to allow for an investigation of the potential for such swelling clays to intercalate organic material and sequester greater amounts of organic carbon relative to other clay minerals.

Three of the sampled soil profiles are part of the Dauerbeobachtungsprogramm of the Hessisches Landesamt für Umwelt und Geologie (Hessian Bureau for Environment and Geology) (see Hessisches Landesamt für Bodenforschung 1998). As part of this program, various chemical, physical and hydrological parameters of soils of different typologies are investigated and documented on a regular basis to monitor changes and trends over time. An up-to-date database of physicochemical parameters for two of the profiles chosen for investigation, Münden 1 (Profile No.: BDF-Mün 1-P5) and Münden 2 (Profile No.: BDF-Mün 2-P4), was available (see Emmerich 1997), allowing some results to be compared for the purposes of validation. Both the World Reference Base for Soil Resources (WRB) (FAO-ISRIC-ISSS 1998) and the German system of soil classification (Bodenkundliche Kartieranleitung (BK)) (AG Boden 1994) were used to characterize the individual soil profiles (see Appendix A for a description of the abbreviated soil horizon designations). Particle size fractions were defined according to German class limits for soil separates and isolated using DIN 19683, Part 2. Figure 2.1 displays the locations of the investigated profiles.

Figure 2.1: Sampling Locations in Hesse, Germany

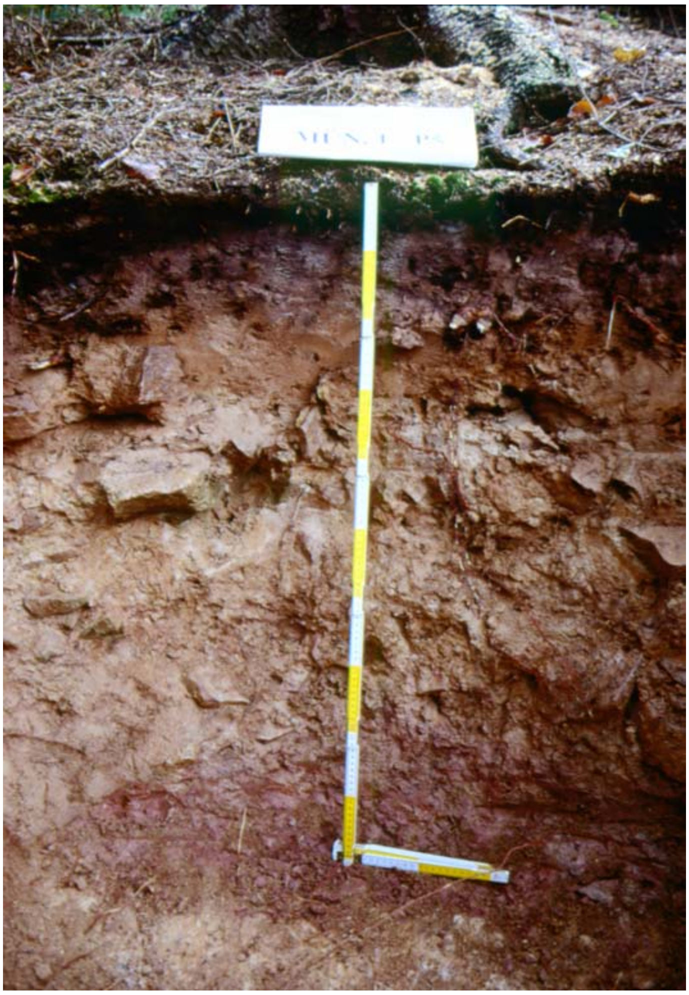


2.1 Soil Profile 1: Münden 1

Sampled in October 2000, the profile Münden 1 is located in the Elsterbach Valley in Reinhardswald, a forest situated in the NE corner of Hesse, close to the town of Münden (Map No. 4523 Münden: R ^{35}41.35, H ^{56}98.42) (see Emmerich 1997). Geologically, the area belongs to the North Hesse *Buntsandstein* (coloured sandstone) region, which was primarily formed from the sedimentary deposition of eroded sand grains and feldspars 233 to 248 million years ago during the Triassic period (Lotz 1995; Emmerich 1997). The site is located in the watershed of the Fulda River, which, together with the Werra, forms the Weser River about 4 km away. There is a precipitation mean of about 700 mm and a mean temperature of 8.0°C in the Reinhardswald annually. According to the WRB (FAO-ISRIC-ISSS 1998), the soil is classified as a slightly stagnic Umbrisol with the beginnings of an albic horizon, otherwise known as a *schwach pseudovergleyte podsolige Braunerde* under the German soil classification system (AG Boden 1994) (see Figure 2.2 for a view of this soil profile). The profile is located on a steep slope at an altitude of about 260 m. The vegetation is mixed, with Norway Spruce (*Pícea abies)* dominating in this forest. An approximate 20% to 30% of the trees are European Beech *(Fagus sylvatica)*. A large Norway Spruce tree is situated directly at the pit, however, contributing to most of the litter. Both loess loam and sandstone were the parent material for the soil at this site. Table 2.1 displays the sequence of horizons for this profile and their observed properties.

The profile itself is 100+ cm in depth and is relatively well-rooted to about 60 cm. The Aeh horizon displays signs of podzolization with vertical variability in organic matter and grey spots indicative of a predominance of residual quartz grains. The soil is very acidic, with a pH ranging from 2.88 for the top few cm to about 3.77 to 3.84 for the subsoil. Not surprisingly, the soil is essentially carbonate free, with values ranging between 0.18 to 0.68% $CaCO_3$. The spruce tree at the pit is likely a contributing factor in terms of the low pH as soils under pine trees tend to be acidic (Tan 2000). Irrespective of vegetation, however, a low pH appears to be common for the soils in the Reinhardswald (see Emmerich 1997). The sampled top 5 cm (Ahe horizon) of mineral soil has a significant amount of total organic matter (TOM) (i.e. about 28%). This reaches a low of about 2% at a sampled depth between 30 and 60 cm (sBv horizon). See Tables B.1-B.5, Appendix B for an overview of basic physicochemical parameters measured for Münden 1.

Figure 2.2: The Münden 1 Profile

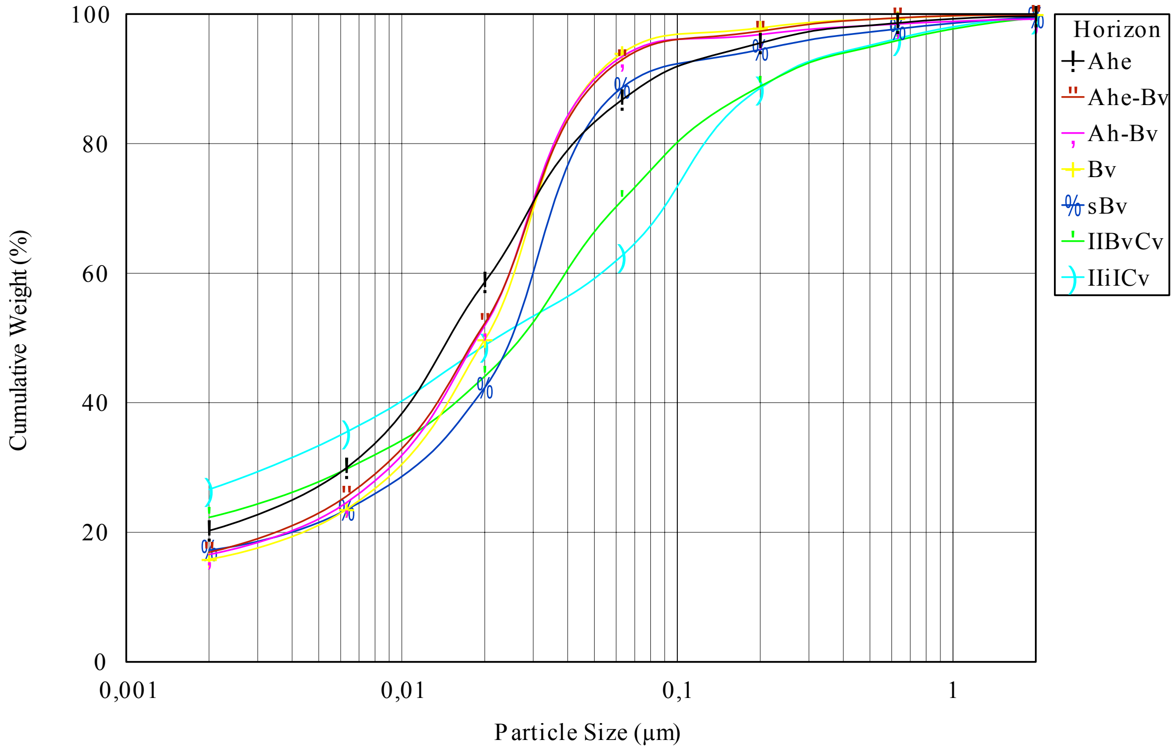


The cumulative particle size distribution of size separates for bulk samples from this profile is shown in Figure 2.3. The soil is primarily comprised of silts down to a depth of about 60 cm. Specifically, silt contents range from 66% for the Aeh horizon to more than 70% for depths between 5 and 60 cm (Ahe-Bv to sBv horizons). Clay varies between an approximate 15 and 20% of the total weight of bulk soil sampled (i.e. <2 mm) for these same depths. The proportion of sand size particles measured for bulk soil samples down to a depth of about 60 cm is relatively small. Below 60 cm, however, both clay (i.e. 20-30%) and sand (i.e. 28-40%) contents by weight increase, with corresponding decreases in the proportion of silt size particles. Samples from a depth of 80-100+ cm contain the greatest amounts of sand and clay in this profile.

Table 2.1: Profile Description of the Münden 1 Profile

Horizon (WRB)	Horizon (BK)	Depth (cm)	Description
O	L	4	primarily pine needle litter
	O	4	
A-E	Ahe	0-5	silt loam, rich in organic matter, brown-black with grey spots, vertical variability in organic matter
	Ahe-Bv	5-10	silt loam, rich in organic matter, dark brown with grey spots
	Ah-Bv	10-20	silt loam, organic rich, Ah spots present, brown
B	Bv	20-30	silt loam, medium brown, medium organic matter content
	sBv	30-60	silt loam, brown with greyish spots, low organic matter content
C	IIBvCv	60-80	silt loam, yellow-red-brown, stony, low organic matter content
	IIilCv	80-100+	loam, reddish brown, eroded sandstone

Figure 2.3: Particle Size Distribution of Bulk Soil Samples (<2 mm) from the Münden 1 Profile



2.2 Soil Profile 2: Münden 2

The soil profile Münden 2 is also situated in Reinhardswald, about 400 m away from Münden 1 (Map No. 4523 Münden: R ^{35}41.22, H ^{56}98.28) (see also Emmerich 1997). Sampled in March 2000, Münden 2 is situated in a monoculture forest consisting of European Beech *(Fagus sylvatica)*, about 220 m in altitude. Like Münden 1, there is a mean annual precipitation amount of about 700 mm and a mean annual temperature of 8.0°C at this site. The soil is a Stagnic Acrisol under the WRB (FAO-ISRIC-ISSS 1998), classified as a *Pseudogley-Parabraunerde* under the German soil classification system (AG Boden 1994) (see Figure 2.4). Although the C horizon is comprised of eroded sandstone, loess loam served as the primary parent material for this soil (see Table 2.2 for a description of the soil profile and the sequence of horizons). This is reflected by the typical yellowish colour of the profile and in the analysis of the particle size distribution of bulk samples. As illustrated in Figure 2.5, there is a dominance of silt size separates throughout the depth of this profile (i.e. >70% of the total by weight). There is a clear increase in the clay content of samples as one moves from the Al to the Bt horizons, indicative of a translocation of clay size particles. The profile exhibits stagnic properties, due to a reduction in total pore volume between the Sw and Sd horizons (Emmerich 1997).

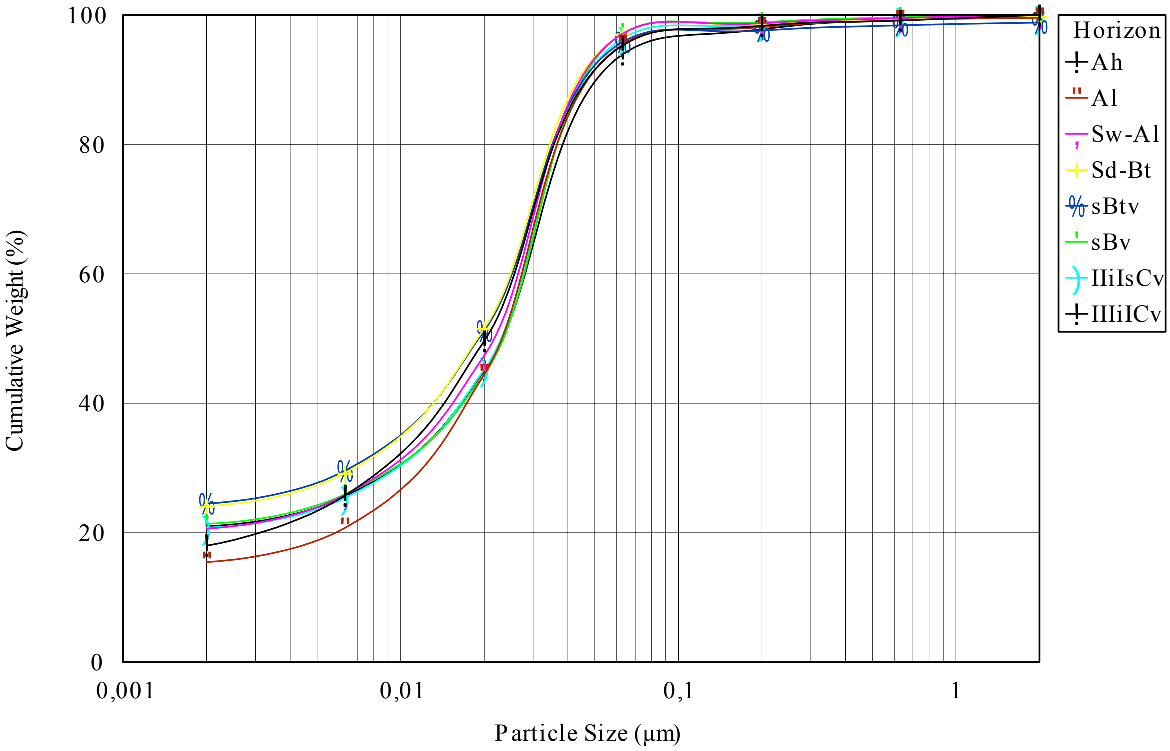
The soil profile is about 160+ cm in depth, with roots being observed as deep as 110 cm. It is also relatively acidic, with a pH ranging from 3.10 for the top 5 cm to about 4.36 at its lowest sampled depth. Carbonate content is also low, varying between 0.21 and 0.78% $CaCO_3$. This is typical for loess-derived soils in middle Europe, where carbonates have been washed out over time (Scheffer and Schachtschabel 2002). Measured TOM is about 20% for the top 5 cm (Ah horizon) of mineral soil. This then declines to about 3.5% at a sampled depth between 5 and 20 cm (Al horizon) and reaches a low of approximately 1.7% for below 110 cm (IIilCv & IIilCv horizons). For an overview of results for the particle size distribution analyses undertaken, as well as other basic physicochemical parameters for this profile, the reader is referred to Tables B.6-B.10, Appendix B.

Figure 2.4: The Münden 2 Profile

Table 2.2: Profile Description of the Münden 2 Profile

Horizon (WRB)	Horizon (BK)	Depth (cm)	Description
O	L	3	primarily European Beech leaf litter
	O	3	
A	Ah	0-5	silt loam, dark brown, high organic matter content
B	Al	5-20	silt loam, yellowish-brown, medium organic matter content
	Sw-Al	20-50	silt loam, yellowish-brown, low organic matter content
	Sd-Bt	50-70	silt loam, yellowish-brown, low organic matter content
	sBtv	70-90	silt loam, yellowish-brown, low organic matter content
	sBv	90-110	silt loam, yellowish-brown, low organic matter content
C	IIilsCv	110-140	silt loam, yellowish-brown, low organic matter content, small amount of sandstone debris
	IIIilCv	140-160+	silt loam, reddish-brown, organic matter absent, weathered sandstone

Figure 2.5: Particle Size Distribution of Bulk Soil Samples (<2 mm) from the Münden 2 Profile



2.3 Soil Profile 3: Königstein

The soil profile Königstein, which was also sampled in March 2000, is located about 4 km SW of the Großer Feldberg in the Taunus Mountains west of Frankfurt am Main, Hesse (Map No. 5716 Oberreifenberg: R ^{34}59.40, H ^{55}62.72). In terms of the geology of the area, this region belongs to the *Rheinisches Schiefergebirge* (the Rhine Shale Mountains) because of the predominance of shales which were formed during the Devonian and Carboniferous periods between 400 and 290 million years ago (Fickel 1974; Lotz 1995). Approximately 520 m in altitude, the profile is situated in a monoculture forest of Norway Spruce (*Pícea abies)*, that receives a mean annual precipitation amount of about 900 mm. The site is relatively cool, with a mean annual temperature of 7.2°C. Under the German soil classification system (AG Boden 1994), the soil is classified as a slightly *podsolige Braunderde* (see Figure 2.6 for a view of this soil profile). This would otherwise be classified as an Umbrisol under the WRB (FAO-ISRIC-ISSS 1998).

Although this profile does not have a distinct eluvial horizon like the Münden 1 profile, vertical variability of organic material in the A horizon indicates the beginnings of podzolization (see Table 2.3 for an overview of the profile and its horizons). The organic horizon is thick and comprised of pine needle litter. The parent material was violet clay shale, combined with loess loam. The profile has a depth of about 105+ cm, with roots visible down to 90 cm. The Königstein profile is also rather acidic, with a pH of 3.20 for the sampled top 5 cm (Aeh horizon) and 3.84 for the bottom of the profile (IViCv horizon). The samples were relatively rich in TOM, with about 29 and 15% for the sampled 0-5 and 5-10 (Ah-Bv horizon) cm, respectively. At a depth of 65-85 cm (IIIBvCv horizon), TOM was still slightly over 3%. Carbonate is virtually absent, ranging between 0.27 and 0.40% $CaCO_3$. Tables B.11-B.15, Appendix B presents the results of physicochemical parameters for this profile.

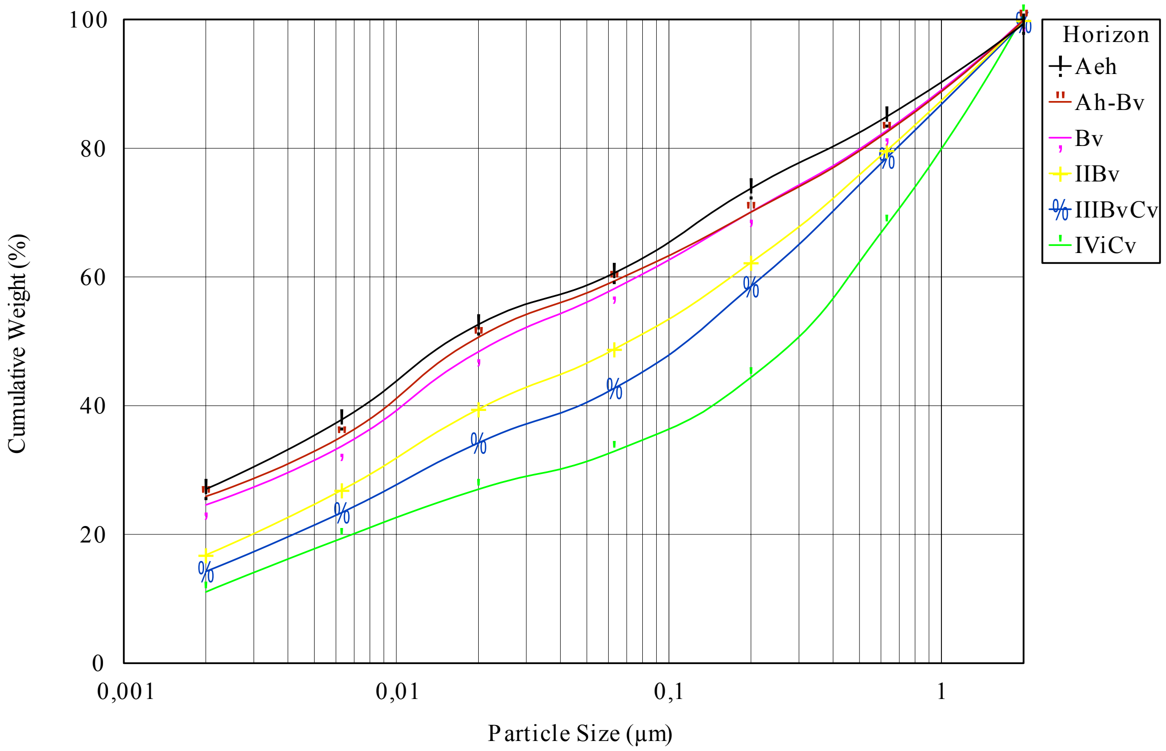
Figure 2.6: The Königstein Profile

Table 2.3: Profile Description of the Königstein Profile

Horizon (WRB)	Horizon (BK)	Depth (cm)	Description
O	L	4	pine needle litter
	O	4	
A	Aeh	0-5	slightly clayey loam, slight podzolization, brown-black, high organic matter content with vertical variability
	Ah-Bv	5-10	sandy loam, medium brown, high organic matter content
B	Bv	10-25	sandy loam, yellowish-brown, medium organic matter content
	IIBv	25-65	very loamy sand, yellowish-brown, very stony, low organic matter content
C	IIIBvCv	65-85	very loamy sand, very stony, high proportion of clay shale debris, yellow-violet in colour, low organic matter content
	IViCv	85-105+	loamy sand, violet clay shale

In terms of soil texture, sand size separates occur in the greatest amounts in bulk soil samples (<2 mm) for all sampled depths (see Figure 2.7). The contribution of sand size particles to the total mass of bulk soils ranges from 39% for the top 5 cm (Aeh horizon) to 68% for the lowest sampled depth of 85 to 100+ cm (IViCv horizon). There were large amounts of shale present below a depth of 20 cm. Due to the tendency of this stone to crumble apart during handling because of its brittleness, sand size contents are likely to be artificially high. Silt particles are the second most prevalent separates, comprising about 22 to 34% of the bulk soil mass. Clays vary from a maximum of 27% for the top 5 cm to a low of 11% for depths below 85 cm.

Figure 2.7: Particle Size Distribution of Bulk Soil Samples (<2 mm) from the Königstein Profile



2.4 Soil Profile 4: Geinsheim

The Geinsheim profile, which was sampled in February 2001, is located at the edge of a gravel pit east of the Rhine River close to Geinsheim in the SW of Hesse (Map No. 6116 Geinsheim: R ^{34}55.90, H ^{55}26.45). This site is situated in a drier, warmer region compared to the other sites, with a mean annual precipitation amount of 600 mm and a mean temperature of 9.5°C. In terms of land use, agriculture dominates in this region which belongs to the *Oberrheingraben* or upper Rhine Valley, a fertile area due to the past deposition of Rhine River sediments. Very little vegetation was growing at this site at the time of sampling, being primarily comprised of grasses. This soil was clearly cultivated in the past, however. Under the German soil classification system (AG Boden 1994), the Geinsheim profile is classified as a *Kolluvisol* overlying a *Pelosol*, which, in turn, is situated on top of a relict *Gley-Tschernosem*. Under the WRB (FAO-ISRIC-ISSS 1998), this soil would be defined as an Anthrosol overlying a Vertisol which, in turn, is situated on top of a relict Gleysol-Chernozem (see Figure 2.8 for a view of this soil profile). Relict Chernozem soils occur on old meander areas of the Rhine River in the upper Rhine Valley, which formed during the dry, warm climate of the Boreal period (Thiemeyer et al. 2002).

Figure 2.8: The Geinsheim Profile

Table 2.4 displays the sequence of horizons and their observed properties. This soil profile contains large amounts of both clay size particles and swelling clay minerals (i.e. smectite), thus, allowing for an investigation of the influence of high clay content and such clay minerals on organic carbon concentrations. Down to an approximate 110 cm, the soil has a distinct dark brownish-black colour that is common to Vertisols. There are signs of past bioturbation in the relict Gleysol-Chernozem (i.e. worm holes). The profile has a depth of about 150+ cm and a pH that falls in the range of alkalinity. Specifically, measured pH values ranged from about 7.34 to 7.79. The top 25 cm (Ap horizon) has a measured TOM of about 7%. Below a depth of 70 cm, the samples have a TOM ranging from 5.5% to a mere 1.2% for the lowest sampled depths. Carbonate contents were also higher compared to the other

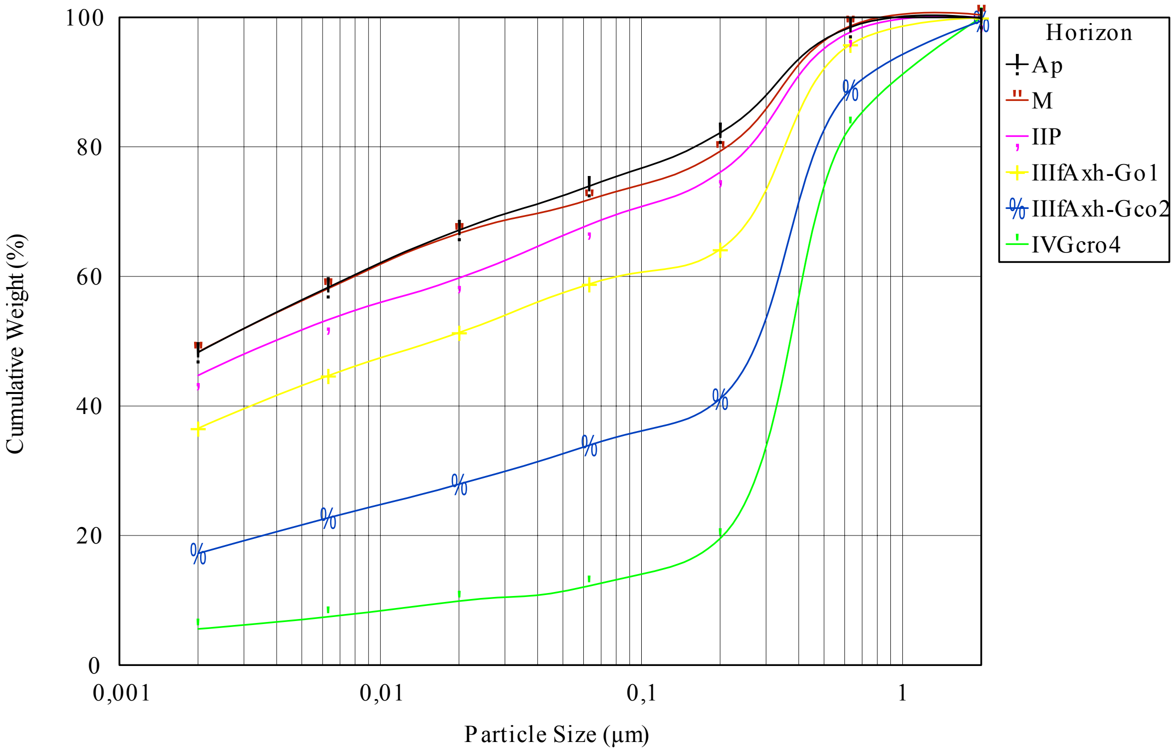
profiles, with 3.82% $CaCO_3$ for the first 5 cm. $CaCO_3$ peaked at a depth of between 110 and 130 cm (IIIfAxh-Gco horizon) with 23.04%. This is clearly reflected by the grey colour of the soil at these depths. See Tables B.16-B.20, Appendix B for an overview of results of basic physical and chemical parameters analyzed for this profile.

Table 2.4: Profile Description of the Geinsheim Profile

Horizon (WRB)	**Horizon (BK)**	**Depth (cm)**	**Description**
A	Ap	0-25	clay, dark brown-black
B	M	25-70	clay, dark brown-black
	IIP	70-90	clay, dark brown-black
	IIIfAxh-Go1	90-110	clay loam, dark grey
	IIIfAxh-Gco2	110-130	sandy loam, carbonate-rich, whitish-grey
	IVGcro4	130-150+	sand, carbonate-rich, brownish-grey

The cumulative distribution of particle size separates for bulk samples is displayed in Figure 2.9. The Geinsheim profile is clay rich down to a depth of 110+ cm. Specifically, whole soil samples contain between 44 and 52% clay by weight to a depth of about 90 cm. At lower depths of between 110 and 150 cm (IIIfAxh-Gco & IIIGcro horizons), however, sand size separates become the most prevalent particles present, varying from 65 to 85% of bulk samples. Clay size separates amount to only 17 and 6% of the total by weight for sampled depths of 110-130 and 130-150 cm, respectively. Silt size particles occur in approximately same amounts, as do clays for these same depths.

Figure 2.9: Particle Size Distribution of Bulk Soil Samples (<2 mm) from the Geinsheim Profile



2.5 Soil Profile 5: Frankfurter Stadtwald

The site Frankfurter Stadtwald was originally sampled in July 1999 and analyzed as part of a project conducted by Jörg Dißelkamp-Tietze (Dißelkamp-Tietze 2000). A more detailed description of this site can be found in this report. This profile is situated in the forest Schwanheimer Wald, SW of the Frankfurt am Main city community Schwanheim, about 92 m above sea level (Map No. 5817, Frankfurt a.M. West: R ^{34}68.89, H ^{55}49.51). The mean annual precipitation is 650 mm and the mean annual temperature is 9.5°C. A mixed forest is present at this site, comprised of European Ash (*Fraxinus excelsior*), Common Oak (*Quercus robur*), European White Elm (*Ulmus laevis*), Small Leaved Lime *(Tilia cordata*), Hornbeam (*Carpinus betulus*), Sycamore (*Acer pseudoplatanus*) and Hedge Maple (*Acer campestre*) trees. The soil is a Gleysol (FAO-ISRIC-ISSS 1998), otherwise known as a *Gley* under the German classification (AG Boden 1994), which formed from floodplain sediments originating from the Main River 6000 to 10 000 years ago (Bargon 1975) (see Figure 2.10 for a photo of this soil profile). The first 80 cm of the profile is comprised of carbonate-free floodplain clay overlying floodplain sand. The pit was dug to the groundwater level, which was about 110 cm in depth at the time of sampling, lower than it usually is over the course of the year. The soil displays hydromorphic properties due to the presence of groundwater, which is often as high as 10-25 cm in the profile (i.e. designated by the symbol G) (see Table 2.5 for a description of the soil profile). Groundwater influences are particularly strong below a depth of 70-85 cm. Similar to the Geinsheim profile, the Frankfurter Stadtwald soil contains large amounts of smectite minerals.

Tables B.21-B.25, Appendix B provides an overview of pH, TOM, carbonate and dry substance contents and the particle size distribution of bulk samples for this profile. The pH of the samples ranged from about 3.65 for the top 5 cm (Ah horizon) to between 5.07 and 5.41 for below a depth of 50 cm (Gro2, Gro3 & IIGr horizons). TOM ranged from 18.82% for the sampled 0 to 5 cm (Ah horizon) to below 2% for a sampled depth of 20-30 cm (Ah-Go & Go horizons). TOM amounts were less than 0.5% for below 85 cm (IIGr horizon). Carbonate contents are low in this profile, with measured amounts varying between a mere 0.18 and 0%.

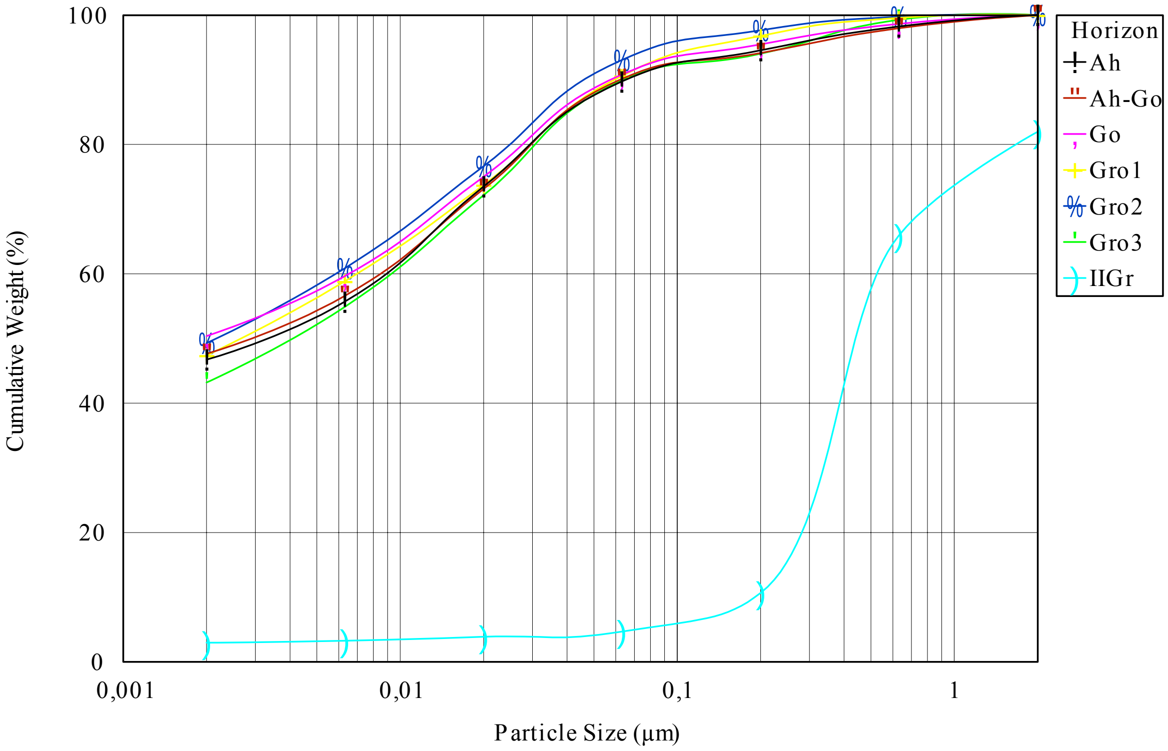
Figure 2.10: The Frankfurter Stadtwald Profile

Table 2.5: Profile Description for the Frankfurter Stadtwald Profile

Horizon (WRB)	Horizon (BK)	Depth (cm)	Description
A	Ah	0-10	silty clay, organic rich, dark brown
	Ah-Go	10-25	silty clay, high organic content, medium brown with rust-coloured spots
B	Go	25-40	silty clay, low organic content, grey-brown with rust-coloured spots, zone of fluctuating groundwater levels
	Gro1	40-50	silty clay, organic matter absent, grey-brown with rust-coloured spots, partially reduced conditions over the course of the year
	Gro2	50-70	silty clay, grey-brown with rust-coloured spots
	Gro3	70-85	silty clay, brown with rust-coloured spots
	IIGr	85-110	sand, dark brown, reduced conditions clearly present (i.e. under water for most of the year)
	Groundwater	110+	

Figure 2.11 displays the cumulative frequency distribution of particle size separates for bulk samples from the Frankfurter Stadtwald profile. This profile contains relatively high amounts of clay size particles. Specifically, clay contents vary from 46% to just over 50% of bulk soil samples by weight to a depth of about 80 cm. Silts are also present in significant amounts, occurring in proportions of between 40 and 46% of the total by weight. Less than 11% of whole soil samples from these same depths are comprised of sand size particles. At lower depths, however, whole soil samples are primarily composed of sand size particles (i.e. >93% by weight). Silts and clays occur in minor amounts at these same depths.

Figure 2.11: Particle Size Distribution of Bulk Soil Samples (<2 mm) from the Frankfurter Stadtwald Profile



3. Methods

The next sections detail the methods used in the preparation and fractionation of bulk samples and the physico-chemical and mineralogical parameters analysed. This will be followed by a brief description of the statistical analyses conducted regarding the soil profiles under investigation.

3.1 Sampling and Sample Preparation

For three of the sites, Münden 1 and 2 and Königstein, pits had already been dug as part of the Dauerbeobachtungsprogramm of the Hessisches Landesamt für Umwelt und Geologie (Hessisches Landesamt für Bodenforschung 1998). For the site near Geinsheim, commercial digging activity at the gravel pit neighbouring the site had already revealed the face of the soil profile. Sampling at these sites, hence, required little preparatory work, merely involving removal of an approximate 10 to 20 cm of soil from the face of each profile to ensure that only fresh, non-weathered samples would be taken. For the profile Frankfurter Stadtwald, a pit was freshly dug down to the groundwater level, about 110 cm in depth (see Dißelkamp-Tietze 2000). After documenting soil profile characteristics, samples were generally taken in 10 cm layers from the bottom of the profile working upward to a depth of 30 cm. Attention was paid to horizon boundaries, with sampling adjusted accordingly to avoid mixing of different horizons. The top 30 cm were sampled in 5 cm layers. Samples were transported in 3 or 6 litre plastic bags, depending on the amount of material taken, and were secured using twist ties to minimize moisture evaporation.

Upon immediate return to the laboratory, about 500 to 1000 g of soil from each sampled depth was placed on plates to be dried at room temperature. Soils generally took an approximate 2 to 3 days to dry completely. Samples were then mixed together according to their horizon for further analysis. If a horizon was greater than 40 cm, it was then split in two, an upper and a lower horizon, and the samples then combined accordingly. The 0 to 5 and 5 to 10 cm depths sampled from each profile were not mixed, to allow for separate analysis.

After drying, samples were then passed through a 2 mm sieve and stored in a refrigerator between 4 and 6°C.

3.2 Particle Size Fractionation

The fine soil samples (<2 mm) were then fractionated in accordance with the German classification scheme for size separates (AG Boden 1994), using a combination of wet-sieving and sedimentation methods. The German classification for particle size separates, which is also shared by other countries in Europe, is somewhat different from that used in the US or as defined by the International Society of Soil Science (ISSS) (see Table 3.1). Unlike the other classification schemes, the German system allows for a more detailed subdivision of both silts and clays.

Table 3.1: Particle Size Fraction Classification Schemes of Germany, US and ISSS

Fraction	**Germany[1] (µm)**	**US[2] (µm)**	**ISSS[3] (µm)**
Sand		very Coarse: 2000-1000	
	coarse: 2000-630	coarse: 1000-500	coarse: 2000-200
	medium: 630-200	medium: 500-250	
	fine: 200-125	fine: 250-100	fine: 200-20
	very fine: 125-63	very fine: 100-50	
Silt	coarse: 63-20	50-2	20-2
	medium: 20-6.3		
	fine: 6.3-2		
Clay	coarse: 2-0.6	<2	<2
	medium: 0.6-0.2		
	fine: <0.2		

[1] see AG Boden (1994)

[2] from US Department of Agriculture (Soil Survey Staff 1975)

[3] from International Soil Science Society (ISSS) (presented in Gee and Bauder 1986)

As only mineral-bound organic carbon was of interest in terms of this study, macroorganic organic matter was first removed using a floatation technique, a method which is commonly used in soil science (see Christensen 1992). For this, an approximate 300 to 400 g of fine soil was placed in a large glass container with about 2 litres of tap water and then rigorously mixed. The macroorganic matter which floated to the top of the water was then removed using a sieve with a mesh-size of 200 µm. This procedure also helped to dissolve larger aggregates. A small portion of the sample (about 3 to 5 g) was set aside to be dried at 100°C for the analysis of bulk soil organic carbon and nitrogen. The rest of the sample was then poured on the top of a series of sieves on a shaking machine (*Retsch AS 200 Digit*) with mesh sizes of 2000 µm - 630 µm, 630 µm - 200 µm and 200 µm - 63 µm to separate the coarse, medium and fine sand fractions, respectively. Tap water was used until it ran clear, indicating a full separation of the finer silts and clays from the sand fractions. The silt and clay size fractions (<63 µm) were collected in a 5 litre container for further separation.

The sand-size fractions were then removed from the sieves and placed on dishes to be dried in an oven overnight at 100°C. The finer <63 µm fractions were dried in large porcelain dishes on sand baths at about 50°C, to ensure that the clay minerals present, notably heat-sensitive smectites, would be left fully intact. After drying, which took about 2 to 3 days on average, the <63 µm fractions were then broken into fragments prior to dispersal. About 10 g of sample was weighed and mixed with 100 ml of deionised water to be dispersed using a probe-type ultrasound (UP 400 S (24 kHz) (*Dr. Hielscher GmbH*)). A soil/water ratio of 1:5 to 1:10 appears to be the most effective in achieving dispersion (Christensen 1992). A S14 probe (diameter of 14 mm) was used for sonication. Samples were treated with 60% of the maximum amplitude for a total of 2 minutes. Those samples which were more difficult to disperse due to a higher clay or organic matter content, were shaken with deionised water and left to pre-soak for up to two hours prior to dispersal. This prevented the need for certain samples to be treated longer or with a greater intensity of ultrasound, hence allowing for consistency in sample treatment. As the application of sonication can produce a considerable amount of heat, requiring the possible use of an ice bath or water cooling jacket to avoid excess heating of samples, a pulse of 0.5 was used to avoid this problem (i.e. energy applied every half second). Additionally, temperatures were monitored to ensure that samples would not get too hot. Chemical methods of dispersion were avoided as this can result in the destruction and dissolution of certain soil minerals (Gee and Bauder 1986).

Ultrasound was only used to disperse the <63 µm fractions, as opposed to the bulk samples, prior to separation using sedimentation. Dispersion using ultrasound has become the most widely accepted method for achieving optimal dispersion and isolation of primary organomineral separates (Edwards and Bremner 1964, 1967; Watson 1971; Anderson et al. 1981; Gregorich et al. 1988; Christensen 1992, 1996). Shaking samples with water is another common method of separation but is known to be ineffective in achieving a disintegration of microaggregates, thus, resulting in incomplete dispersion (Christensen 1992). With sonication, the flocculation of particles, particularly clays, is limited in the resultant suspension during sedimentation. Further, this method is highly effective for soils high in organic matter and clay content and is not likely to destroy primary particles or alter the crystal lattice of minerals if applied properly (Gee and Bauder 1986; Moore and Reynolds 1997; Gregorich et al. 1988). Care in its application is required, however, as it may cause a shift in organic matter from one fraction to another. Notably, macroorganic matter may be broken down, causing a shift from sand size to smaller silt and clay size fractions, when ultrasound is applied to bulk soil samples (Balesdent et al. 1991). This can be avoided by only applying ultrasound to the silt and clay size separates, as was done here. A migration of organic matter between individual size fractions is less likely to occur with the smaller silt and clay size fractions as the organic matter present is more intimately bound to minerals (Christensen 1992).

Once dispersed, the samples were then put into sedimentation cylinders and filled up to the 1 litre mark using deionised water. Several cylinders (5 on average) were used per sample to ensure that enough material would be obtained from each fraction to carry out all analyses. The individual silt and the clay size fractions were then sampled at the appropriate depth and time using a pipette after the calculated time passed using Stokes' law for the viscous drag on a sphere as follows:

$$V = \frac{r^2 g(D_s - D_f)}{18V_f}$$

where V is the particle velocity in cm s^{-1}, r is the equivalent radius of the particle in cm, g is the gravitational acceleration (i.e. 980 cm sec^{-2}), D_s is the density of solid in g cm^{-3} (assumed to be 2.65 g cm^{-3}), D_f is the fluid density in g cm^{-3} and V_f is the fluid viscosity at temperature t in g cm^{-1} s^{-1}. The pipette method used, referred to as the Köhn method (see DIN 19683, Part 2), involved the use of special apparatus which allows for quick sampling of many samples simultaneously, with a minimum of sample disturbance. Specifically, the pipette is attached to an apparatus on the wall, which, with the aid of rollers, can be glided from cylinder to cylinder with ease. The pipette, which is lowered into the sample with the aid of a lever, is closed at the bottom but has three small holes near the end to reduce sample stirring while pipetting. Aliquots of the sample (10 ml) are then removed with the pipette using underpressure created with an attached hand-operated pump.

The cylinders were shaken head-over-head for at least 30 seconds prior to each size fraction being sampled. The silt size fractions were sampled and defined according to the German classification as listed in Table 3.1. Clay particles were sampled in terms of coarse (<2 µm) and fine clay (<1 μm). The cut-off point of 1 μm for fine clays, as opposed to the official limits of 0.6 or 0.2 μm, was chosen due to the limitation of the method used (i.e. sedimentation). For a more accurate separation of the 0.6 or 0.2 μm fraction, centrifugation is required and the equipment used needs to be exactly calibrated to ensure that this fractionation between such fine particle sizes is achieved. The method and distinction used here, however, was considered sufficient given the goals of this study.

Upon fractionation, the silt and clay particle size fractions were then placed in an oven overnight at 50°C. The samples were then carefully ground using an agate mortar and pestle to ensure homogenisation for the subsequent analyses.

3.3 Analyses Conducted

3.3.1 Basic Physicochemical Parameters

A number of basic physicochemical parameters were measured for bulk soil samples to characterize the soils under investigation. First, dry content was determined gravitimetrically on fresh soil samples upon arrival at the laboratory according to the DIN 38 414, Part 2. After soils were dried at room temperature and passed through a 2 mm sieve, pH using a solution of 0.01 M $CaCl_2$ (DIN 19684, Part 1) and loss-on-ignition (i.e. total organic matter (TOM)) using dry combustion at 550°C (DIN 19684, Part 3) were determined. For the measurement of carbonate content, the DIN 19 684, Part 5 was not used as this requires the use of equipment that is not appropriate for soils that contain very little carbonates (i.e. Scheibler apparatus). Rather, carbonate content was determined coulometrically using a Coulomat 702-SO/CS/W (*Ströhnlein Instruments*). For this, an approximate 100 to 250 mg of sample was weighed in a small vessel and treated with about 2 ml of a 1:1 solution of H_3PO_4 (42%) and 0.1 N $AgNO_3$. After oxidation, carbonate content was then determined according to the amount of energy required to back titrate a solution of $Ba(ClO_4)_2$ to its original electric potential.

The potential cation exchange capacity (CEC_{pot}) was determined for four of the sampled profiles, Münden 1 and 2, Königstein and Geinsheim, according to Mehlich (DIN 19 684, Part 8). This method involves the use of a buffered $BaCl_2$ solution (pH 8.1) to flush the exchangeable base cations Ca, Mg, K, Na into solution, where their concentrations are then measured using AAS (AAnalyst 300 (*Perkin Elmer*)). H^+ concentrations were determined by titration with HCl. CEC_{pot} was unfortunately not measured in prior analyses of the Frankfurter Stadtwald profile and was, thus, unavailable for comparison.

The effective cation exchange capacity (CEC_{eff}) was conducted for the acidic soils, Münden 1, Münden 2 and Königstein, using an adapted version of Mehlich (DIN 19 684, Part 8) with a non-buffered solution of $BaCl_2$ (pH 5.1). Using this method the exchangeable cations Al, Fe and Mn were measured with flame AAS (AAnalyst 300 (*Perkin Elmer*). H^+ concentrations were determined by titrating extracts with NaOH. It was not necessary to measure the cations Ca, Mg, Na and K, as their values would not be different from those estimated using the Mehlich method for CEC_{pot}. CEC_{eff} was not analysed for the Geinsheim profile as the soil pH fell in the range of alkalinity (see Table B.16, Appendix B). Again, data for the Frankfurter Stadtwald profile was unfortunately not available.

Particle size analyses were also conducted for each sampled depth or composite sample according to the DIN 19 683, Part 2. Prior to fractionating the bulk samples using both sieving and sedimentation techniques, samples were first treated with a 15% solution of H_2O_2 to eliminate organic matter. A 0.4 N solution of sodium pyrophosphate ($Na_4P_2O_7$) was added to samples to achieve dispersion.

The content of Fe in crystalline and amorphous oxides was measured for all bulk soils using the Na-dithionite-citrate-bicarbonate extraction method of Mehra and Jackson (1960). Several samples from the Frankfurter Stadtwald soil profile were mixed together according to horizon to limit their number for analytical purposes. Extracts were measured using flame AAS (AAnalyst 300 (*Perkin Elmer*)). In this method, ferric ions are reduced at the low redox potential caused by dithionite. This causes the crystal oxide structure to become destabilized, releasing the Fe atoms to solution where they complex with citrate anions to prevent precipitation. Although this method is commonly used prior to the x-ray identification of clay minerals to eliminate the interference of oxides (Moore and Reynolds 1997), a test was first conducted on a sample of bentonite from Bavaria, Germany to ensure that smectites would not be destroyed. As clay minerals also contain Fe, their destruction would, of course, lead to elevated measured concentrations of this metal ion. After being treated using this method, the bentonite was washed several times using a centrifuge (at 4000 rpm for 5 minutes) and deionised water. The sample was then mounted on a glass slide and measured using a Philips

PW 1710 equipped with a CuKα tube from 2.3 to 20° 2θ (34 kV, 28 mA). The x-ray reflection indicated that montmorillonite in the sample remained intact after this treatment.

Oxalate-extractable Fe, Al and Mn (DIN 19684, Part 6 modified from Tamm (1932)) in bulk samples were also determined. This method measures the content of short-range, poorly ordered and amorphous oxides. It involves the use of NH_4-oxalate at a pH of 3.25, with extraction in the dark at room temperature. Again, a *Perkin Elmer* AAnalyst 300 was used for analysis.

3.3.2 Organic Carbon and Nitrogen Analyses

Carbon (OC) and nitrogen (N) analyses were conducted on both bulk soil samples (<2 mm) and the individual particle size fractions using an Elemental Analyser EuroEA 3000 (*HEKAtech GmbH*), which has a detection limit of 0.01%. Analyses are based on the principle of dynamic flush combustion, coupled with gas chromatography. Samples were first homogenized using an agate mortar and pestle. As only organic carbon, and not total, was of interest, samples were first treated with HCl to eliminate carbonates. For this, about 10 to 20 mg of sample was weighed in silver capsules and then carefully treated with 20 µl of a 20% HCl solution. The samples were then dried overnight in a Teflon rack in an oven at 70°C to eliminate the HCl. Preceding measurement, about 10 to 20 mg of the catalyst vanadium pentoxide (V_2O_5 (99.9%)) was added to each of the silver capsules and then closed. With the aid of an automatic sampler, samples were then oxidized in the presence of high concentrations of O_2 with a furnace temperature of 1070°C. Helium was used as the carrier gas. The resultant gases NO_x, CO_2 and H_2O were passed through a reduction reactor containing copper to bind excess O_2 and convert NO_x products to N_2. H_2O was filtered out with a trap containing magnesium perchlorate. With about 100 ml He/min, the gas mixture was then lead through a GC column at an oven temperature of 40°C where the gases are separated. Measured concentrations were then analysed with a thermal conductivity detector. Peak area estimates were calculated with the software program CallidusTM (*HEKAtech GmbH*).

In addition to samples which yielded unusual or unexpected results every 5th sample was measured twice. The calculated mean of the two measurements were taken as the final result. For each sample series measured (about 30 to 40 samples), two blanks were measured, one silver capsule that was treated with HCl and one containing V_2O_5 only. The standard used was 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (BBOT (*HEKAtech*)), with 72.52 % C and 6.51 % N. Along with two BBOT standards measured with each sample series, a soil standard (Soil 1, *HEKAtech*) containing 3.5% C and 0.216% N was also analysed three times to ensure equipment stability and validate the accuracy of results (i.e. at the beginning, in the middle and at the end of each series).

3.3.3 Specific Surface Area

Specific surface area (SSA) was measured for the finer silt- and clay-size fractions. Organic matter or carbon tends to be sorbed or is more closely associated with the surface of the finer silts and clay particles (Christensen 1992, 1996), the association of which being the fundamental focus of this study. The method applied to measure SSA was an adapted version of that developed by Carter et al. (1986), which employs the use of ethylene glycol monoethyl ether (EGME ($CH_3CH_2OCH_2CH_2OH$)), otherwise known as 2-Ethoxyethanol. It is presently popular to use N_2 and the Brunauer-Emmett-Teller (BET) equation to estimate SSA (see Carter et al. 1986). This method was deemed inappropriate, however, due to its potential to yield misleading results. Specifically, N_2 does not enter the internal layers of smectites and, thus, only provides an estimate of external surface area (Carter et al. 1986, Theng et al. 1999). As the interlayer of these minerals can contribute up to 90% of the total SSA, the use of N_2 could yield significant underestimates for samples containing smectites. At the same time, the EGME method may yield slight overestimates of the surface area of samples, as EGME molecules may cluster around cations at the mineral surface, resulting in a greater than monolayer coverage at these sites (Goldberg et al. 2000). A slight overestimation was considered more acceptable though than a severe underestimation of SSA for those soils containing smectites.

Although it has been suggested that reasonable results can be obtained using the EGME method without prior treatment of samples to eliminate organic matter (Cihacek and Bremner 1979), samples are best stripped of organic material prior to analysis. It can be expected that the presence of significant amounts of organic matter, notably in topsoils, can lead to false results of SSA. Many investigators have found that SSA significantly increases after the removal of organic matter (see Theng et al. 1999). This may be due to blockage of micropores or organic coatings on particles or aggregates, reducing the amount of surface area measured.

Further, EGME is likely to partially partition into the organic phase, leading to an elevated amount retained by the sample without prior treatment, yielding SSA results that are too high given the mineral composition of the clay fraction. To avoid this problem, and to ensure consistency in the treatment of samples, samples were first stripped of organic material prior to analysis.

The use of H_2O_2 may cause some crystals of micaceous and smectitic clays to be damaged (Theng et al. 1999). Peroxidation is known to dissolve some Fe oxides and all Mn oxides (Olson, Thompson and Wilson 2000). To ensure the appropriateness of H_2O_2 to eliminate organic matter, tests were first conducted on bentonite samples from Bavaria, Germany. For this, about 1 to 2 g of bentonite were treated with 10%, 15% and 30% solutions of H_2O_2 in an acidic milieu (i.e. a pH set at 4-5 using 5% HCl) over a period of 3 days on a sand bath at 70°C. Carbonates would be destroyed during this process. Samples were then dried, mounted on glass slides and analysed using x-ray diffractometry to determine whether montmorillonite minerals in the bentonite remained intact. A 30% H_2O_2 solution lead to the partial destruction of these swelling minerals, as evidenced by a considerable weaker first-order reflection compared to that for untreated bentonite. A 10% H_2O_2 solution did not, however, result in any significant alteration of the first-order x-ray reflection. This was, thus, used for the further treatment of samples. Again, treatment involved the use of a sand bath at 70°C and the addition of just enough 5% HCl to achieve a pH of between 4 and 5. H_2O_2 was continuously added and the samples heated until conspicuous effervescence had stopped and the solution had become clear in colour, indicating completion of oxidation. Once this process was complete, samples were centrifuged at 1800 to 2000 rpm for 15 minutes, decanted and the supernatant liquid discarded. Deionised water was then added to the samples, stirred and centrifuged again at the same speed and time. This process was repeated three times to ensure complete removal of salts. Samples were then dried at 60°C in an oven and then carefully ground using an agate mortar and pestle.

H_2O_2-treated samples were then placed in a desiccator containing approximately 200 g of phosphorous pentoxide (P_2O_5). After removing air from the desiccator with the aid of a vacuum pump (for 30 min. at 0.80 mbar), the samples were left to dry for a minimum of two days to ensure complete desiccation. About 100 to 800 mg of dried sample, depending upon sample availability, was then weighed into small 10 ml weighing vessels with air-tight lids. These vessels had also been placed in the desiccator with P_2O_5. EGME was then added to the samples using a pasteur pipette to create a soil-adsorbate slurry with an excess of adsorbate. This was done as quickly as possible and the lids placed securely on the weighing vessels to ensure moisture absorption was kept to a minimum. This is especially necessary given the fact that atmospheric moisture competes with EGME for adsorption sites on the clay surface (Theng 1974), potentially yielding misleading results. Samples were then left for 30 minutes to allow the EGME to penetrate all particle surfaces. The samples were placed in a desiccator containing 200 g of free calcium chloride ($CaCl_2$), which was previously dried in an oven at a temperature of 210°C for about 2 hours. It is often recommended that a vessel with a mixture of $CaCl_2$ and EGME also be placed in the desiccator to maintain a higher vapour pressure (e.g. about 20 g EGME with 120 g $CaCl_2$) (Carter et al. 1986). This supposedly supports the formation of a monomolecular layer on particle surface areas, without which EGME losses would be greater than a monolayer equivalent resulting in lower measured SSAs. This was initially done here but was found to be troublesome. With the inclusion of this solvate, equilibrium took considerably longer to be reached. This meant that samples were handled more often, enhancing the potential for mistakes to be introduced into the analytical process. Carter et al. (1986) suggest themselves, in fact, that its inclusion is not completely necessary as excess EGME will automatically migrate from the samples to the free $CaCl_2$ to form a solvate of the two. Excess EGME was simply added to samples to increase its concentration in the desiccator.

Once placed in the desiccator with the lids off, a piece of aluminium foil was loosely placed over the samples to prevent any potential splattering that may occur during evacuation. A total of two desiccators were used simultaneously to increase the number of samples which could be treated at one time. The pump, attached to the desiccator with a rubber tube, was then turned on for 1 hour with an underpressure of 0.80 mbar. A flow-through container with $CaCl_2$ was attached between the desiccator and the pump to entrap excess EGME. This also helps to remove water from the air entering the desiccator upon release of the vacuum and, thus, minimizes sample moisture uptake.

After an hour, the desiccator was closed, the vacuum pump turned off and the samples left overnight to equilibrate. Samples were weighed the next morning, their weights recorded, and then immediately returned to the desiccator. The desiccator was evacuated again for another hour using the vacuum pump. The samples were then left for 2 to 4 hours before being weighed again. This process was repeated until sample weights remained stable over two weightings, indicating that excess EGME had been evaporated and that monolayer coverage of particle surface had been achieved. This generally took about 4 weightings (i.e. a total of 2 days) for most sample weights to become stable. No more than 12 samples in total using two desiccators were treated at any one time. If too many samples are placed in a desiccator simultaneously, equilibrium takes too long to be reached. The $CaCl_2$ was changed after every two series of samples treated (i.e. every week).

SSA was then calculated using the formula:

$$A = W_{EGME}/(W_s \times 0.000286)$$

where A= SSA ($m^2\ g^{-1}$), W_{EGME} is the weight of EGME retained by the sample in g, W_s is the weight of the sample in g and 0.000286 is the weight of a monolayer of EGME on a square meter of surface (see Carter et al. 1986).

Using values for SSA and the OC contents of the silt and clay particle size fractions for the profiles under investigation, the OC loadings of mineral surfaces were calculated as follows:

OC loading ($mg\ m^{-2}$) = SSA ($m^2\ g^{-1}$) / OC content ($mg\ g^{-1}$).

From this, we can estimate the extent to which mineral surfaces are covered by organic material.

3.3.4 X-ray Diffraction

Only the <2 µm clay size fraction isolated from bulk soils was analysed using x-ray diffraction (XRD), as this fraction yields the best reflection for the identification of all clay minerals present in samples. Minerals falling into the larger size particle fractions were not of interest in terms of this study. A total of 10 mg of each clay size fraction isolated was weighed in 3 ml glass vials. About 30 drops of deionised water were then added to each vial using a pasteur pipette. The samples were sonicated to disperse the clay particles, a method which is strongly recommended to achieve good preparations for XRD analysis (Moore and Reynolds 1997). This was done using a probe-type ultrasound (UP 400 S (24 kHz) (*Dr. Hielscher GmbH*)) with a probe tip size of 3 mm, which is appropriate for small sample volumes. A pulse of 0.6 and an energy level of 30% of the maximum amplitude over a period of 30 to 90 s was generally sufficient to achieve dispersion.

The glass slide method was used to prepare samples (see Moore and Reynolds 1997). Using a pasteur pipette, the dispersed samples were carefully dropped on glass microscope slides of 18 x 18 mm. About 35 to 40 drops of sample can generally be placed on a glass slide without spillage. Care was taken to ensure that all of the sample was placed on the glass slide so that the same amount of material (i.e. 10 mg) would be analysed for all samples, allowing for increased reliability in making cross-comparisons between XRD reflections (i.e. to allow for comparisons regarding the relative amounts of individual clay minerals in the various samples from each respective soil profile). Samples generally took about 24 hours at room temperature to fully dry prior to analysis. Diffraction analyses were conducted using a Phillips PW 1710 instrument equipped with a Cu Kα tube. A voltage of 34 kV and a current of 28 mA were applied for analysis. The divergence slit was set at 1° and the receiving slit at 0.2. A step size of 0.010° 2θ and a count time of 2.5 s per step was generally used and samples were measured from 3 to 40° 2θ, the range within which the most important clay mineral reflections appear.

Those samples determined or suspected to contain smectite minerals were then exposed to ethylene glycol, one of the most common methods used to determine the presence of swelling clays (Brown and Brindley 1980; Moore and Reynolds 1997). For this, the same glass specimens were placed on a rack above an approximate 50 ml of ethylene glycol in an air-tight glass container. The container was then put in an oven for two days at 60°C. The samples were analysed with the same program settings as before to detect the swelling behaviour of the minerals present in the samples. Two days were generally sufficient for most samples to fully swell. Some, however, required longer or did not respond that well to treatment (i.e. not all glycol-solvated smectites yielded a d(001)-spacing of 16.9-17.1 Å).

Although soils from Königstein were initially suspected to contain smectite minerals, prepared samples did not respond to ethylene glycol solvation, indicating that the reflection(s) in the range of 14 Å were due to the presence of chlorite, vermiculite and/or interlayer complexes. Several Königstein samples (i.e. to a depth of 45 cm) were then heated to 300°C for an hour to detect changes in the reflections and provide additional information regarding the types of clay minerals present. Vermiculite, for instance, typically collapses to 10 Å at these temperatures (Brindley and Brown 1980; Moore and Reynolds 1997).

After solvation had confirmed the presence of smectites in the Geinsheim profile, a Greene-Kelly test (see Moore and Reynolds 1997) was also conducted to determine smectite type (i.e. montmorillonite, saponite, nontronite or beidellite). This was also done for two samples from the Frankfurter Stadtwald profile, as this had not been previously determined. In this test, several ml of a 0.5 M LiCl solution were added to about 20 mg of sample to saturate the smectites with Li ions. This is believed to neutralize the charge of the octahedral sheet, causing montmorillonite to form a mineral similar to pyrophyllite which does not respond to treatment using ethylene glycol, water or glycerol. The samples were then shaken head-over-head overnight. Samples were washed on the following day with deionised water and centrifuged at 3800 rpm for 10 minutes to eliminate chloride. Samples were then mounted on glass slides in a manner similar to the other prepared samples and were analysed using 28 mA and 34 kV from 2.3 to 10° 2θ.

For the identification of the individual XRD reflections and a semi-quantitative analysis of the relative amounts of the individual minerals present in the clay fraction, the program MacDiff (*Dr. Rainer Petschik, J.W. Goethe-Universität Frankfurt am Main*) was used. Peak occurrence was corrected for using the pattern for quartz present in samples (i.e. the 26.65° 2θ). As quartz is ubiquitous in soils, and its peak positions do not vary for it does not undergo any significant atomic substitutions in its structure, quartz can conveniently be used as a built-in internal standard (Moore and Reynolds 1997).

3.3.5 Statistical Analyses

A statistical model was set up using the program *SPSS for Windows* (Version 10.0) to analyse the relationships between the following variables and measured OC and N contents, and the ratio thereof, for bulk soils and individual silt and clay particle size separates for each profile:

- % of sand, silt and clay in bulk soils
- Particle size separate
- Exchangeable cation saturation
- Clay mineral composition of the clay fraction
- Specific Surface Area (SSA)
- Na-dithionite-citrate-bicarbonate and oxalate-extractable Fe, Al and Mn

Statistical correlations (two-sided Pearson coefficients) and r^2 values were calculated for the measured variables for each profile separately to isolate those factors which may play a role in the stabilization of organic matter in the individual soils. An attempt was made to analyse the A horizon in isolation from the B and C horizons of the respective soils when possible. For parameters measured only on bulk soils, however, the sample size was not large enough to allow for a satisfactory analysis of separate horizons. In these cases, the whole soil profile was the focus of analysis.

4. Analytical Results

In the next sections, the results for the physico-chemical and mineralogical parameters analyzed for both bulk and fractionated soils will be presented for each soil profile. Statistical relationships observed between the various parameters will be discussed in Chapter 5.

4.1 Organic Carbon and Nitrogen Contents and C:N Ratios

Results regarding the OC and N contents of samples will be first presented for bulk soils for all profiles. This helps provide an overview of the organic matter dynamics for each of the soil profiles according to depth and allows for comparisons to be made regarding the differences between them. This will then be followed by a discussion of the results for the fractionated samples for each soil profile.

4.1.1 A Comparison of Bulk Soils for All Profiles

As shown in Figure 4.1, bulk samples from the Frankfurter Stadtwald profile contain the greatest amounts of OC in the top layers of the profile, with 137.00 g OC kg^{-1} (see Tables C.1, C.4, C.7, C.10 and C.13, Appendix C) for the raw results of analyses. This is likely due to larger plant litter inputs to this soil compared to the other profiles. OC amounts rapidly decrease with depth, however, reaching levels similar or lower than that found in the other soils at depths below 40 cm (i.e. <5 g OC kg^{-1}). Bulk samples from the top 5 cm of the Münden 1 and 2 and Königstein forest profiles also have relatively high amounts of OC (i.e. 62-74 g OC kg^{-1}), while the A horizon of Geinsheim profile has the lowest observable concentrations (i.e. 20.84 g OC kg^{-1}). Given the little vegetation growing at this site, this is not surprising. OC amounts measured for bulk soils from this site are, however, significantly greater compared to that for the other soil profiles at depths between about 25 and 90 cm. At lower depths, OC concentrations begin to converge for all profiles.

N concentrations measured for bulk soils show a similar pattern (see Figure 4.2). Bulk soils from the topsoil of the Frankfurter Stadtwald profile contain the greatest amount of N (i.e. 9.79 g N kg^{-1}). The soils Münden 1 and 2 and Königstein have N amounts in the range of 3-4 g N kg^{-1} for the top 5 cm, while whole soils from Geinsheim have the lowest concentrations (i.e. 2.19 g N kg^{-1}). N concentrations for the Frankfurter Stadtwald profile decline the most rapidly, generally reaching levels that are the lowest observed for all profiles at lower depths (i.e. 0.00-0.50 g N kg^{-1}). Similar to OC concentrations, bulk samples from Geinsheim contain the greatest amounts of N at depths of between approximately 25 and 70 cm (i.e. 0.82-1.48 g N kg^{-1}). N concentrations are generally comparable between profiles at lower depths.

Values of the ratio of C:N for bulk soils are displayed in Figure 4.3. As shown, bulk soils from Münden 2, Königstein and Frankfurter Stadtwald exhibit C:N ratios that fluctuate between 10 and 20 down to depths of about 25 cm. This is typical for these soil types (see AG Boden 1994). Topsoil samples from Geinsheim have measured C:N ratios that are lower (i.e. <10), while bulk soils from Münden 1 have the highest ratios (i.e. 20-30). The higher C:N ratios exhibited by Münden 1 samples from the upper layers are expected for soils that display signs of podzolization (AG Boden 1994). The fact that topsoil samples from Königstein do not have similar ratios of C:N suggests that podzolization processes are not as advanced for this soil profile. Ratios of C:N rapidly fall below 10 for the Münden 1 soil, likely a reflection of a higher proportion of humic acid in the organic fraction. Bulk soils from the Frankfurter Stadtwald profile exhibit rather large fluctuations at depths lower than about 50 cm. Many samples have, in fact, measured ratios larger than 20, especially at the depths of greater than approximately 80 cm. This is likely due to the groundwater influences at this site, which create anaerobic conditions at these depths for a large part of the year, inhibiting the mineralization of organic matter. A C:N ratio of > 25 is expected for gleyic soils such as the Frankfurter Stadtwald soil profile (AG Boden 1994).

Figure 4.1: OC Contents (g kg^{-1}) of Bulk Soils (<2 mm) for all Sampled Profiles as a Function of Depth

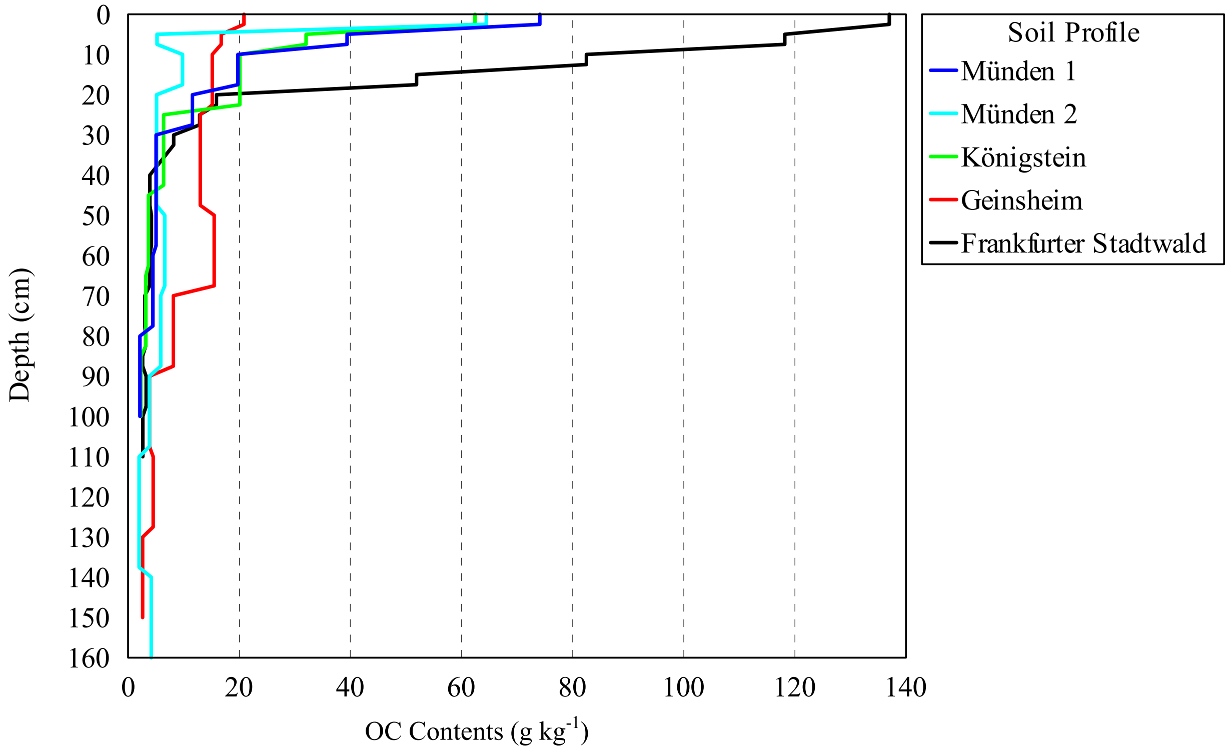


Figure 4.2: N Contents (g kg^{-1}) of Bulk Soils (<2 mm) for all Sampled Profiles as a Function of Depth

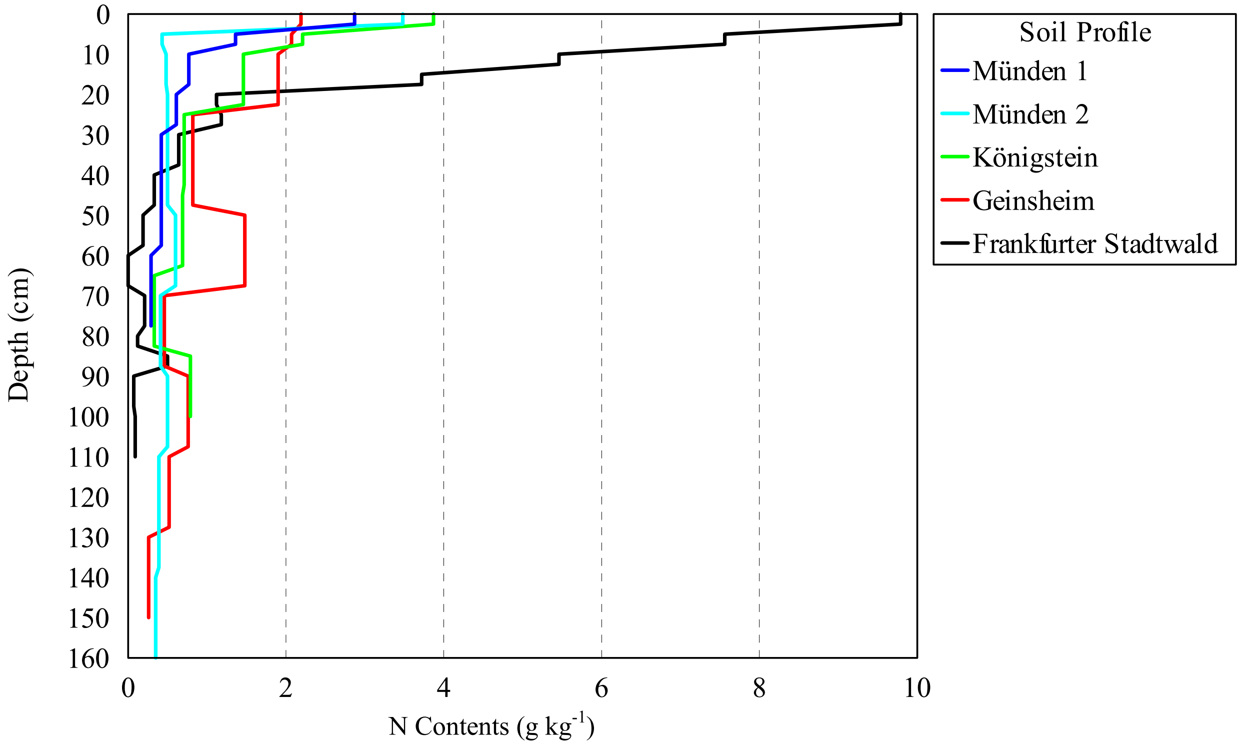
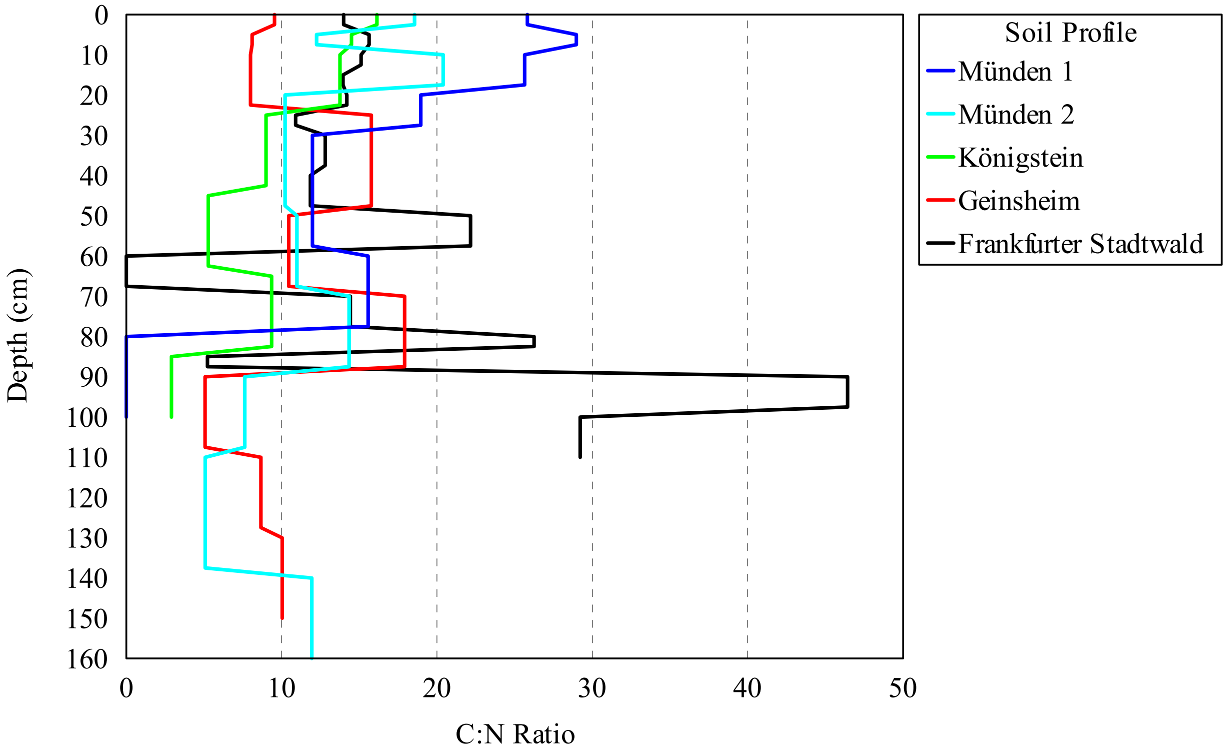


Figure 4.3: C:N Ratios of Bulk Soils (<2 mm) for all Sampled Profiles as a Function of Depth



4.1.2 Profile 1: Münden 1

OC and N concentrations for the individual particle size fractions isolated from Münden 1 whole soil samples are displayed in Figures 4.4 and 4.5. Ratios of C:N are shown in Figure 4.6. In the interest of simplicity, only the silt and clay size fractions are displayed, the size separates of greatest interest to this study. For a closer examination of results for OC and N for all size fractions, including sand, readers are referred to Tables C.2 and C.3, Appendix C. The smaller particle size fractions, the silts and clays, contain significantly greater amounts of OC than the sand size separates in this soil profile. The clay fractions, for instance, contain as much as 164.63 g OC kg^{-1} at a sampled depth of 0-5 cm, compared to <10 g OC kg^{-1} for the sand size separates for the same depth. Greater amounts of OC are generally associated with the smallest particle size fractions, notably the fine silt and coarse and fine clay separates, throughout the depth of the Münden 1 profile.

The coarse silt fractions have significantly lower concentrations of OC at all sampled depths. OC contents range from as much as 107.78 to 2.22 g kg^{-1} and 151.04 to 9.74 g kg^{-1} for the coarse silt and fine clay fractions from depths of 0-5 cm and 80-100+ cm, respectively. For samples taken between 0 and 20 cm, the fine silt and coarse clay fractions analyzed contain higher OC concentrations than the fine clay fractions. Below 30 cm, however, the greatest amounts of OC are associated with the fine clay fraction. At a depth of 80-100+ cm, for example, the fine clay fraction contained 9.74 g OC kg^{-1}.

Similarly, larger amounts of N are associated with the silt and clay size fractions than with the sand size separates. For instance, concentrations for the coarse sand size fractions vary from 0.35 g N kg^{-1} for samples taken from 0-5 cm to 0.12 g N kg^{-1} for the lowest sampling depths. In contrast, N contents for the fine clay fractions range from 7.95 to 1.23 g kg^{-1} for these corresponding depths, respectively. The fine clay fraction generally contains the greatest N concentrations for most sampled depths, which leads to a lower C:N ratio for this size separate compared to the fine silts and coarse clays.

Figure 4.4: OC Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Münden 1 Profile as a Function of Depth

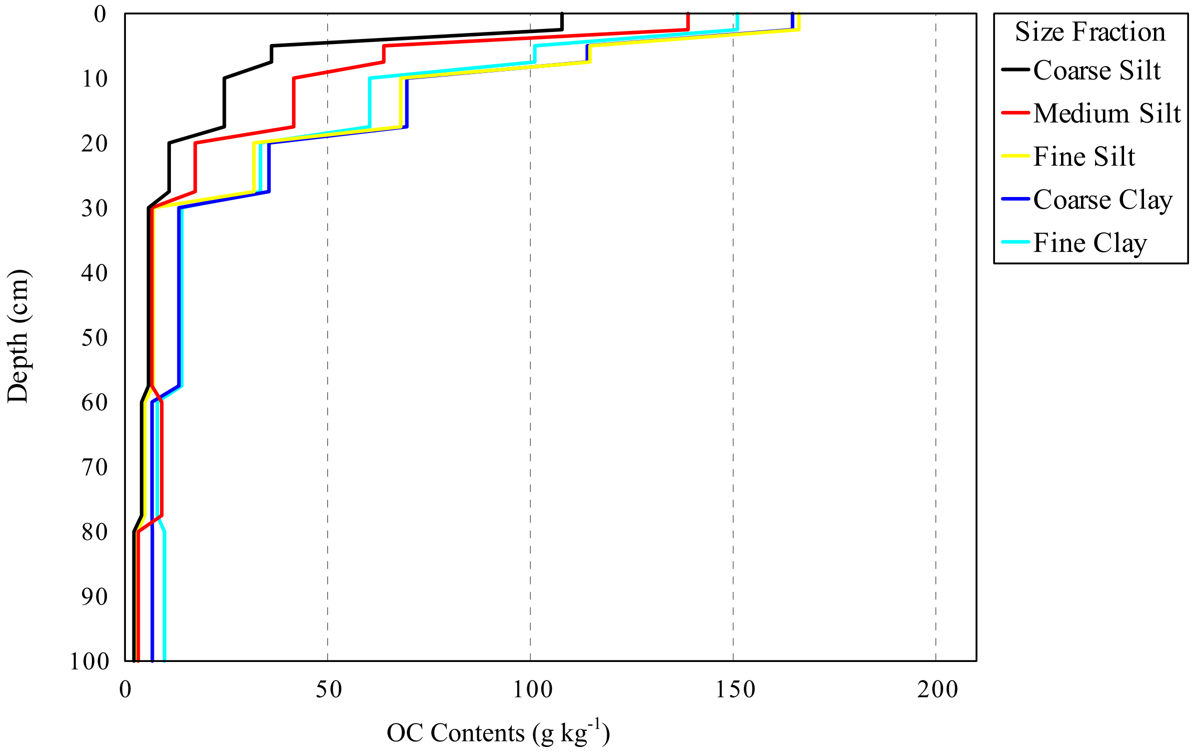


Figure 4.5: N Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Münden 1 Profile as a Function of Depth

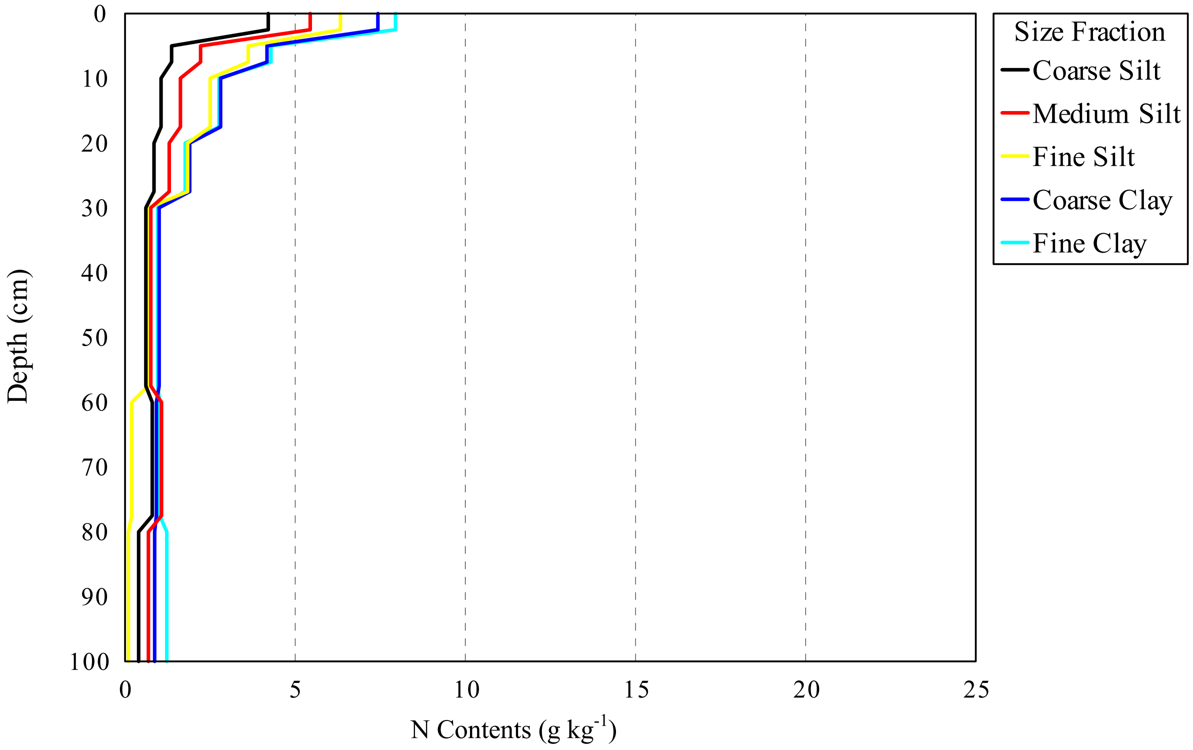
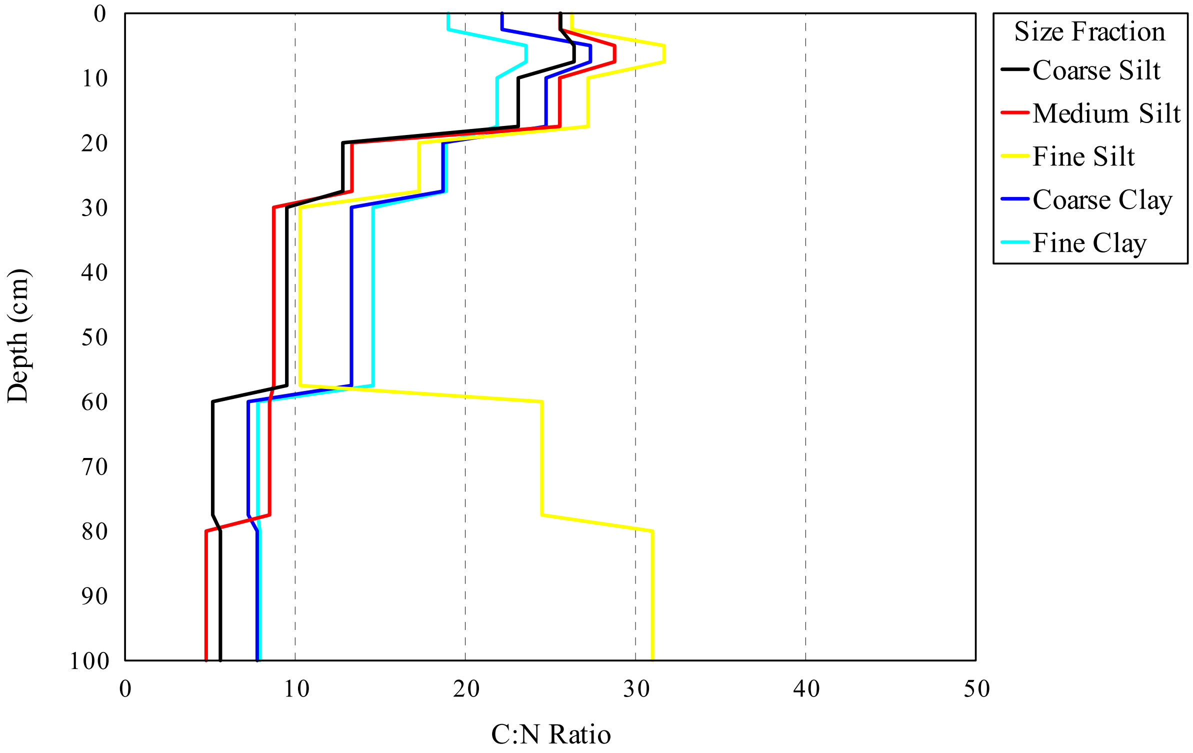


Figure 4.6: C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Münden 1 Profile as a Function of Depth



All particle size fractions, including the sand size separates, have comparable C:N ratios for samples from a depth of 0-5 cm (i.e. 20 to 30). While C:N ratios decline rapidly for the sand size separates below this depth, however, values remain rather high for the silt and clay fractions to a depth of 20 cm (i.e. 19 to 28). At lower depths (i.e. below 30 cm), the relative amount of C:N decreases for most size fractions. There is an observed increase in the ratio of C:N for the fine silt fractions below 60 cm due to low N concentrations compared to the other size separates. Although the ratio of C:N was similar for all particle size separates for samples taken from 0-5 cm, the ratios for the finer silt and clay fractions did not decrease to the same extent as that for the sand size fractions at lower depths. For instance, the C:N ratio of the silt and clay size fractions for depths of between 10 and 20 cm still remained in the range of 20 to 30, whereas that for sand was about half as much for the same depth (i.e. between 10 and 15). This suggests a protective role for the smaller particle size fractions; that is, organic matter associated with silts and clays takes longer to be degraded than that found in the sand size fractions.

4.1.3 Profile 2: Münden 2

The OC and N contents and C:N ratios for the silt and clay size particle fractions of samples from Münden 2 as a function of depth are displayed in Figures 4.7, 4.8 and 4.9, respectively. The raw results for the sand size separates can be seen in Table C.5, while the data for silts and clays are presented in Table C.6, Appendix C. OC and N contents for all particle size separates decrease with depth. Again, the sand size separates analyzed contain significantly lower amounts of OC than that measured for the silt and clay size fractions. For instance, OC concentrations for the coarse sand fraction vary from 11.53 to 1.16 g kg^{-1} for sampled depths of 0-5 and 140-160+ cm, respectively. For the fine clay separates, in contrast, OC ranges from 200.79 to 5.36 g kg^{-1} for the same depths, respectively. Of the smaller size separates, the fine silt and clay size fractions consistently contain significantly larger amounts of OC relative to the coarser silt fractions from Münden 2. For the top 5 cm of the profile sampled, contents range from 170.85 to 200.79 g OC kg^{-1} for these fine fractions compared to 78.53 and 131.79 g OC kg^{-1} for the coarse and medium size silt fractions, respectively.

Figure 4.7: OC Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Münden 2 Profile as a Function of Depth

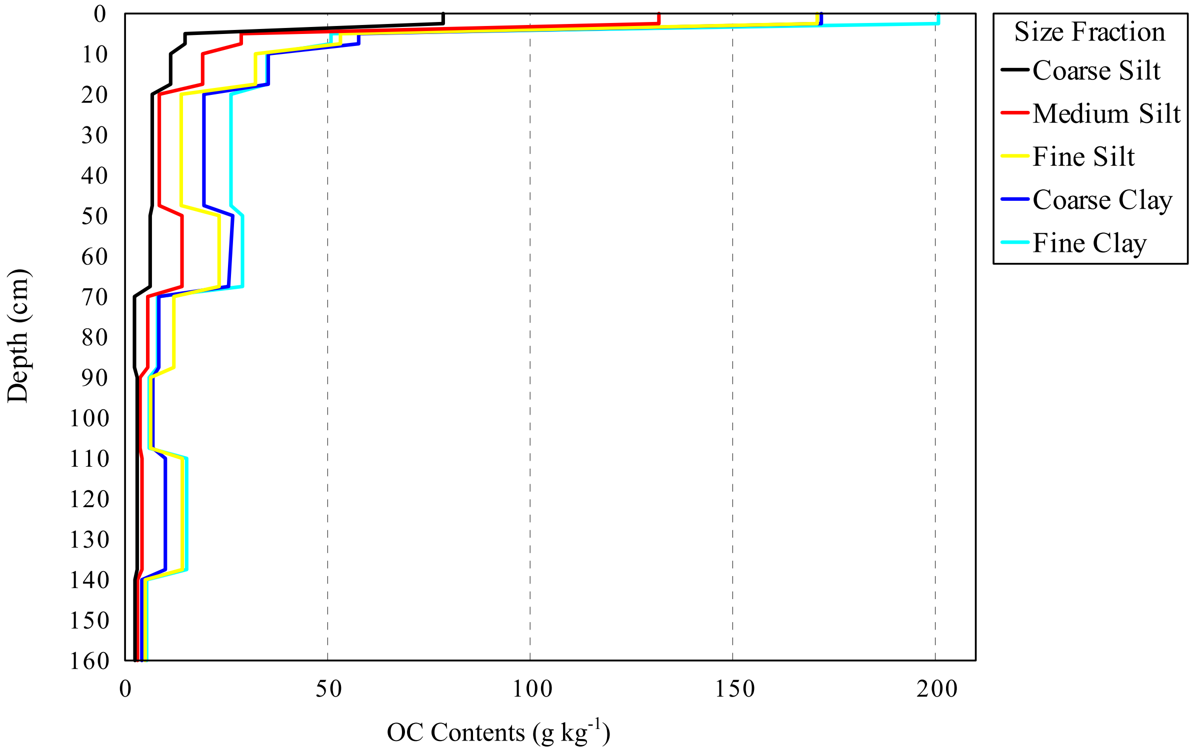
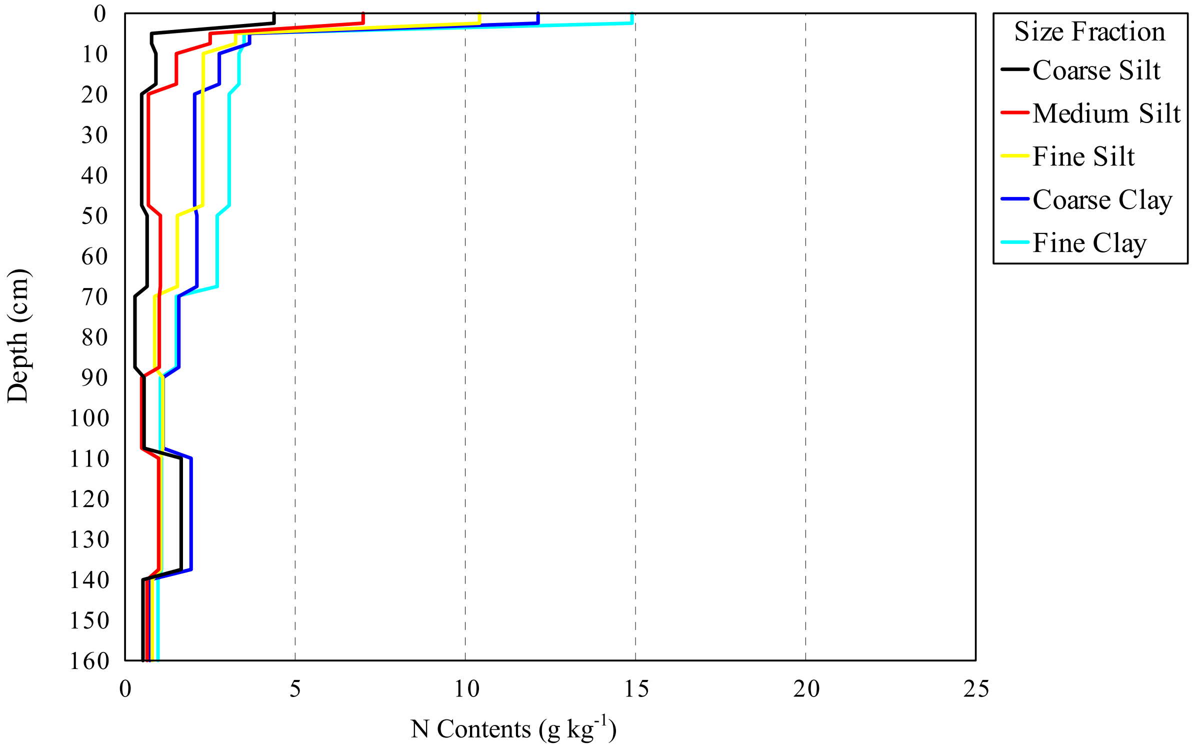


Figure 4.8: N Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Münden 2 Profile as a Function of Depth

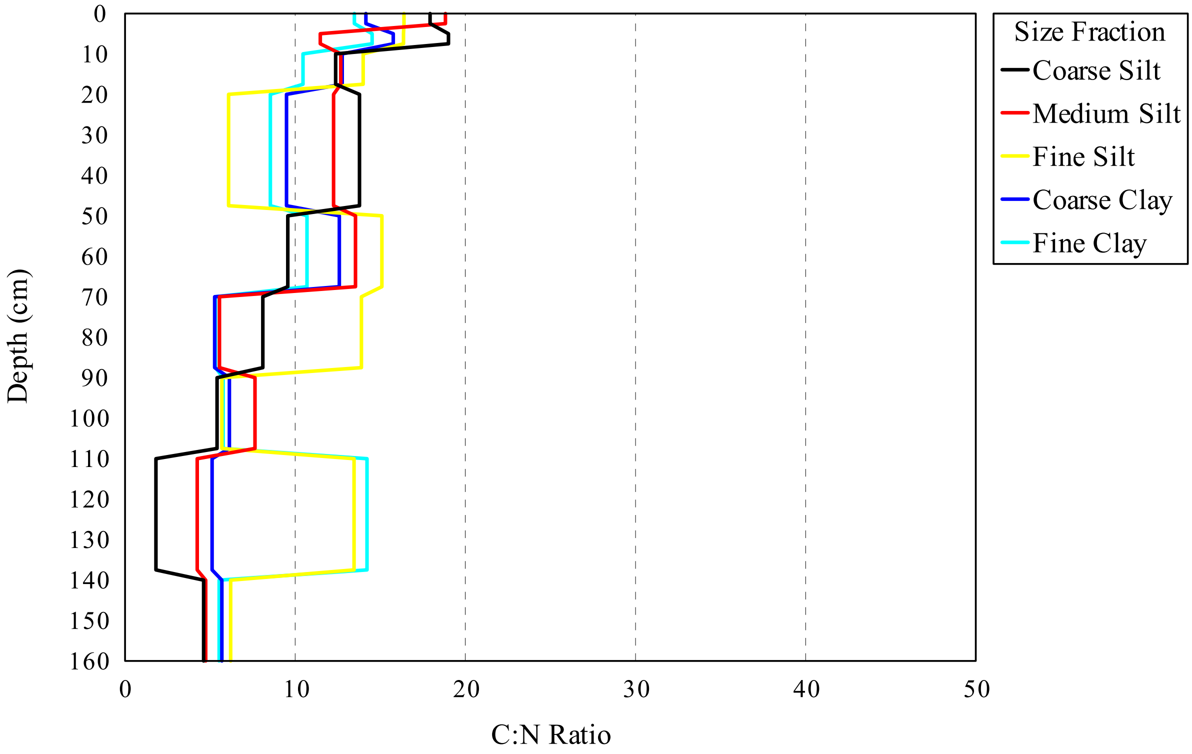


With the exception of samples taken from a depth of 50-70 cm, OC progressively decreases with depth for all fractions. The fine silt and clay size separates from a sampled depth of 50-70 cm generally have greater OC contents than the same fractions from depths of 20-50 cm. This may be due to an increase in clay particle content at this depth due to the transport of clay particles, together with bound organic material, from the above Al horizon. At the lowest sampled depth of 140-160+ cm, the OC content does not substantially differ between the individual particle size fractions compared to other depths, with about 2.45 g OC kg^{-1} for the coarse silt fraction to 5.36 g OC kg^{-1} for the fine clay fraction.

N concentrations measured for the particle size fractions follow a similar pattern, with greater amounts being associated with the silts and clays than with the sand size separates. N contents range from 0.66 to 0.37 g kg^{-1} for a sampled depth of 0-5 cm to 0.35 to 0.23 g kg^{-1} for depths of 140-160+ cm for all sand size separates. In comparison, the coarse clay fractions, for instance, have measured concentrations of 12.14 and 0.73 g N kg^{-1} for the same sampled depths, respectively. Among the smaller particle size separates, N concentrations follow a similar pattern as OC, with the fine silt and clay size fractions containing the greatest amounts. For the top 5 cm, the coarse silt fraction contains 4.38 g N kg^{-1} while the fine clay fraction has 14.90 g N kg^{-1}. N then progressively decreases for most fractions with depth, and the differences between the individual size fractions begin to narrow. For samples taken at depths of 140-160+ cm, N contents range from only 0.53 g kg^{-1} for the coarse silt fraction to 0.97 g kg^{-1} for the fine clays.

In terms of the ratio of C:N, the coarser silt fractions generally have a higher ratio compared to the finer silt and clays to a depth of 50 cm, possibly reflecting less degraded forms of organic material associated with these fractions. The C:N ratio generally ranges between 10 and 20 for these depths. Below 70 cm, the C:N ratio falls below 10 for most size separates. Between 110 and 140 cm, the fine silt and clay size fractions display an increase in the C:N ratio. This is due to an enrichment of OC in these size separates relative to the other fractions at these depths, a possible reflection of sample inhomogeneity (e.g. the presence of root fragments).

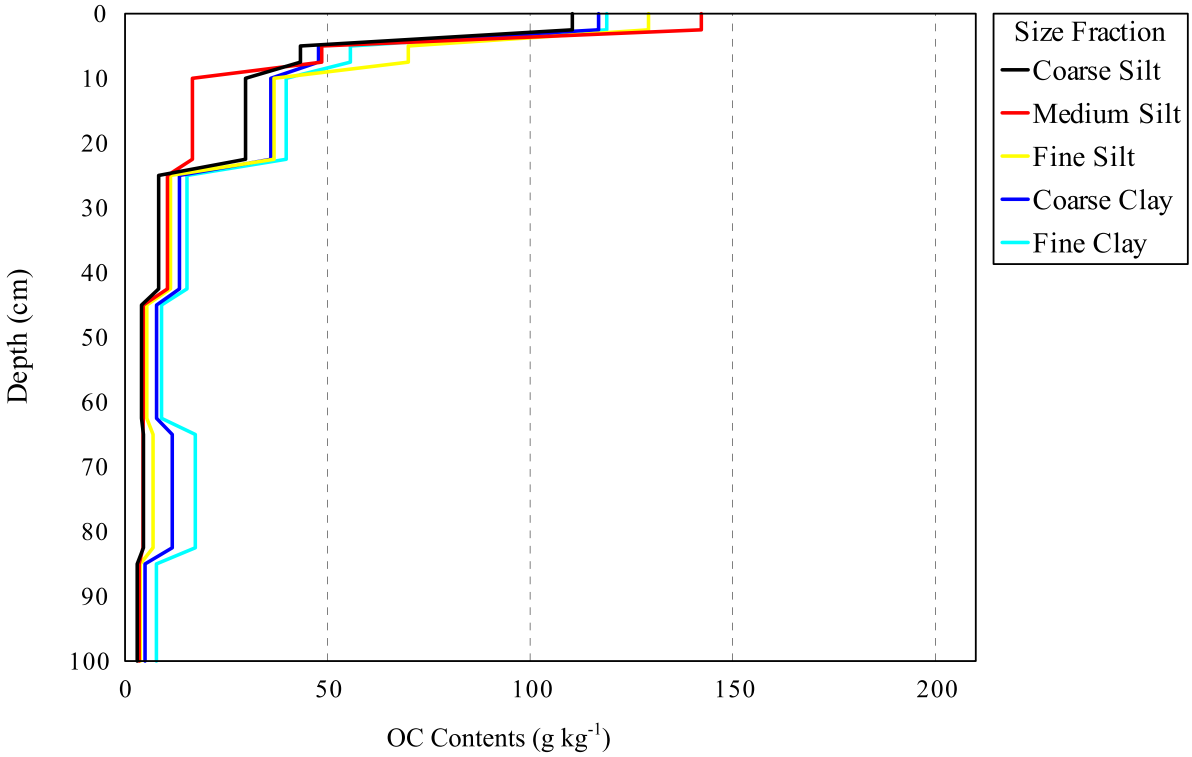
Figure 4.9: C:N Ratios of the Silt and Clay Size Fractions (<63 μm) from the Münden 2 Profile as a Function of Depth



4.1.4 Profile 3: Königstein

The results of OC and N analyses for the silt and clay size particle fractions are depicted in Figures 4.10, 4.11 and 4.12. Values for sand are not depicted but can be referred to in Table C.8, Appendix C. Table C.9, Appendix C displays the raw data for silts and clays. Both OC and N contents for all particle size fractions decline with depth as organic material becomes increasingly mineralized. Compared to the smaller size silt and clay separates, however, measured concentrations for the sand fractions do not decrease with depth to the same extent. Overall, the silt and clay size fractions have considerably greater amounts of OC and N than that found for the sand size separates. With the exception of samples from the top 10 cm of this profile, OC contents progressively increase with decreases in particle size, peaking in the fine clay fraction with each sampled depth. In the top 5 cm, the medium silt fraction contains the greatest amount of OC with 142.25 g kg^{-1}, while the highest OC concentrations at a depth of 5-10 cm are associated with fine silts (i.e. 69.93 g OC kg^{-1}). OC contents generally decrease for all fractions with depth, with the exception of samples taken from a depth of 65-85 cm. Here, there is an increase in OC, especially for the two clay fractions. Specifically, the coarse and fine clay fractions have OC contents of 7.81 and 9.0 g OC kg^{-1} at a depth of 45-65 cm, respectively. This increases to 11.64 g OC kg^{-1} for coarse clays and 17.34 g OC kg^{-1} for fine clays between 65 and 85 cm.

Figure 4.10: OC Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile as a Function of Depth



N concentrations are considerably higher in the silt and clay samples compared to the sand size fractions. Among the silts and clays, the highest concentrations are associated with the smallest particle size fraction, the fine clay fraction, for all sampled depths. Amounts range from 8.67 g N kg^{-1} for the top 5 cm to 1.44 N kg^{-1} for the lowest depth of 80-100+ cm. With the exception of samples from a depth of 65-85 cm, where coarse and medium silts contain more N, coarse clays contain the second greatest amount of N at all sampled depths. Similar to OC content, measured N for the fine clay fraction from a depth of 65-85 cm is unusually high, with a value of 4.27 g N kg^{-1}.

Figure 4.11: N Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile as a Function of Depth

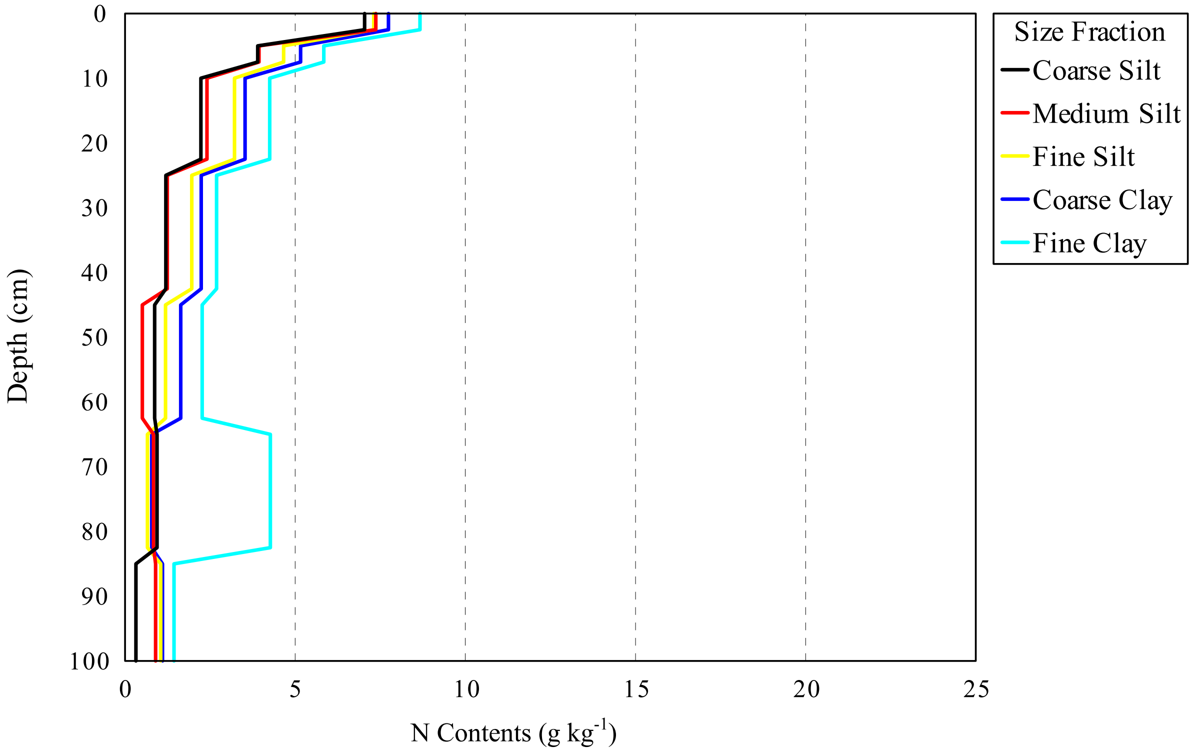
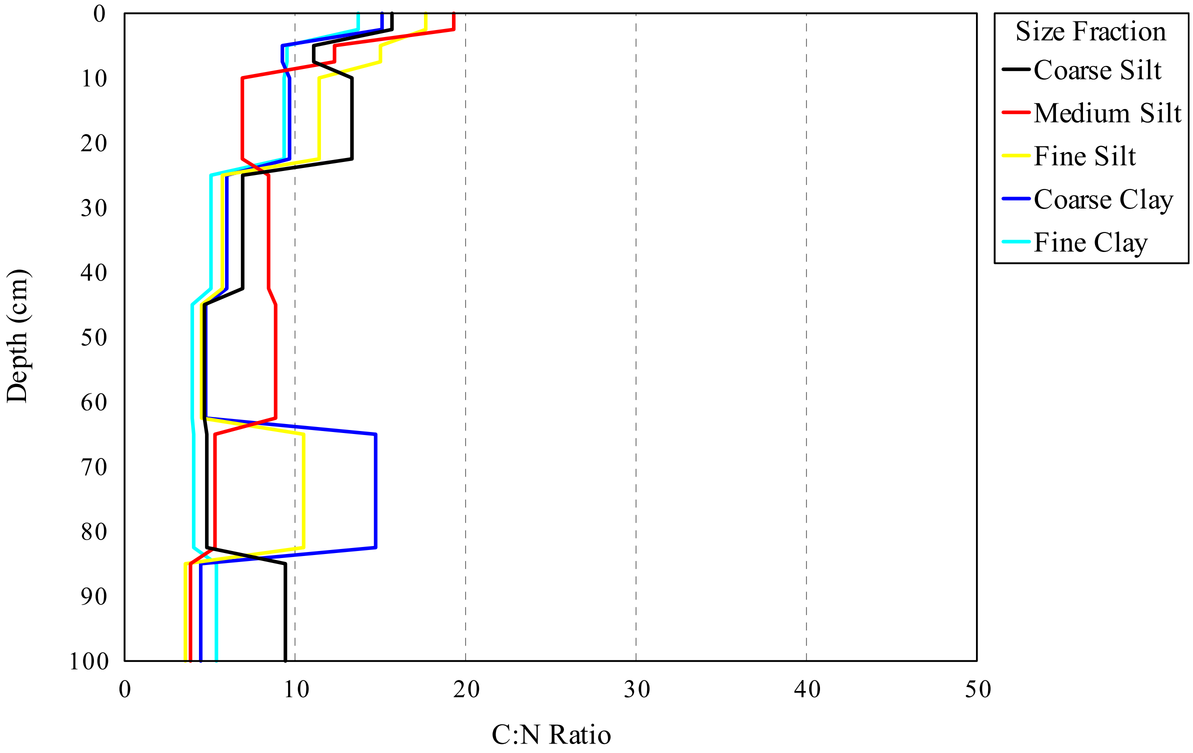


Figure 4.12: C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile as a Function of Depth

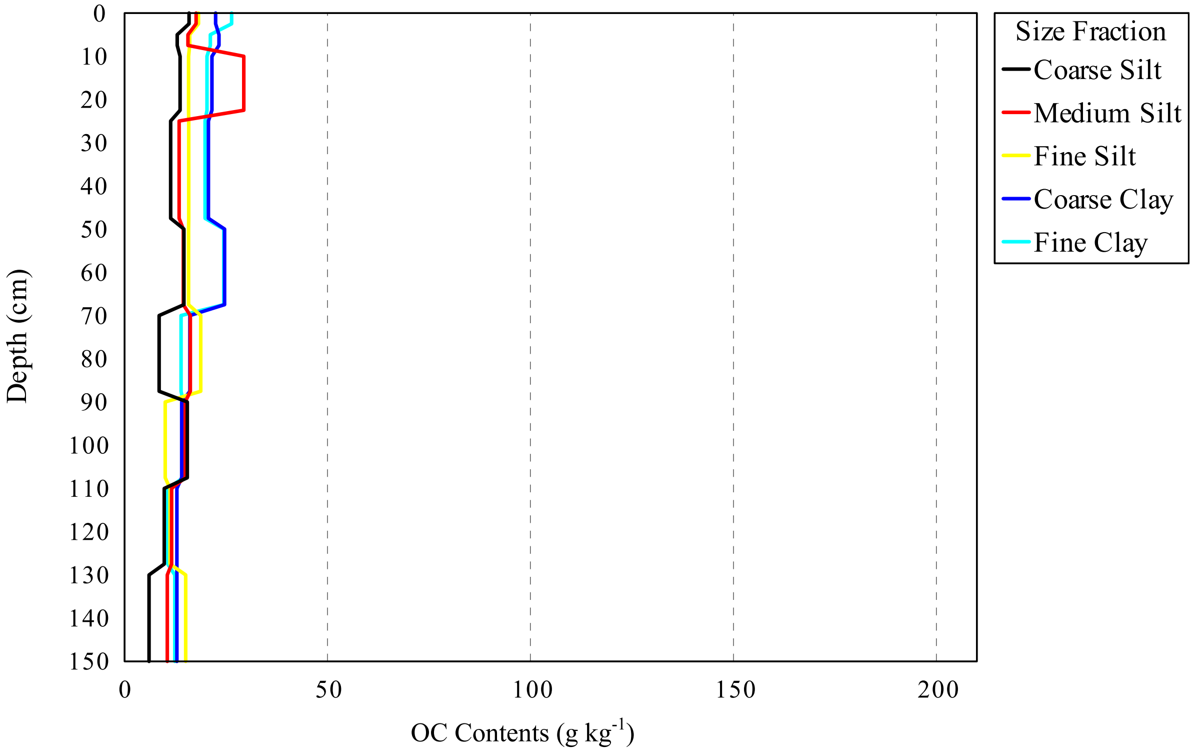


Ratios of C:N for the sand size fractions isolated from 0-25 cm are often higher than that observed for silts and clays (i.e. 16-39). This is likely due to the presence of less degraded particulate organic matter present in these size fractions. The ratio of C:N for the silt and clay fractions ranges from 14 to 19 and 9 to 15 for depths of 0-5 and 5-10 cm, respectively. This ratio then sinks to below 10 for most silt and clay fractions below a depth of 10 cm. With the exception of samples from 10-25 cm and depths of greater than 85 cm, the fine clay fraction generally has the lowest C:N. This is due to an enrichment of N for this fraction.

4.1.5 Profile 4: Geinsheim

Figures 4.13 and 4.14 present the OC and N amounts measured for the silt and clay size particle separates for Geinsheim, respectively. The ratios of C:N are shown in Figure 4.15. The raw results for both OC and N, together with the calculated ratios of C:N, are given in Tables C.11 and C.12 in Appendix C. Compared to the silt and clay size fractions, the sand size samples contain less OC. OC ranges from 24.11 to 5.65 g kg^{-1} for all three sand size separates from a depth of 0-5 cm. This decreases to between 1.11 g kg^{-1} and 0.59 g kg^{-1} for the lowest depths. For silts and clays, OC varies between 15.90 and 26.40 g kg^{-1} to 6.07 and 15.08 g kg^{-1} for the sampled 0-5 and 130-150 cm, respectively. Considering only the silt and clay size separates, greater amounts of carbon are associated with the clay size fractions to a depth of about 70 cm, with the exception of a sampled depth of 10 to 25 cm (i.e. medium silts contain 29.39 g OC kg^{-1}). For instance, OC contents range from 22.45 g C kg^{-1} for the coarse clay fraction (i.e. 0-5 cm) to 24.65 g C kg^{-1} at a depth of 50-70 cm. Interestingly, OC contents do not decrease significantly with depth to about 50 cm. Between 50 and 70 cm, OC amounts, in fact, increase for all fractions. For example, OC concentrations increase from 11.36 g kg^{-1} for the coarse silt fraction and 19.84 g kg^{-1} for the fine clay at a depth of 25-50 cm to 14.62 g kg^{-1} and 24.44 g kg^{-1} for these two fractions at a depth of 50-70 cm, respectively. This corresponds to a significant increase in the clay content at these depths (see Table B.20, Appendix B). OC contents then decrease at a depth of 70-90 cm for the fine particle size separates (e.g. to 8.51 g kg^{-1} for the coarse silt fraction and 13.93 g kg^{-1} for the fine clay fraction). In contrast, concentrations of OC associated with the sand size fractions increase at these depths (e.g. OC contents of the coarse sand size fraction increase from 1.52 g kg^{-1} at 50-70 cm to 6.60 g kg^{-1} at 70-90 cm). Where the relict Chernozem occurs, there does not appear to be a clear pattern in terms of the relationship between particle size and OC content; that is, that increasing amounts of OC are associated with decreases in particle size. Some of the coarser silt fractions contain more or equivalent amounts of OC compared to the finer clay fractions at these depths (e.g. at 110-130 cm, medium silts contain 11.61 g OC kg^{-1} compared to 10.66 g OC kg^{-1} for fine clays). This is perhaps due to groundwater influences at these depths.

Figure 4.13: OC Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile as a Function of Depth



Similar to OC concentrations, the greatest N concentrations are associated with the finer particle size fractions, notably fine silts and clays. For instance, while coarse sand contains 0.90 g N kg^{-1} for the first 0-5 cm sampled, the coarse and fine clay size fractions have a measured 3.01 and 2.29 g N kg^{-1}, respectively. At a depth of about 25-70 cm, where N becomes virtually absent for measured sand size separates, N varies from a high of 2.69 to a low of 1.15 g kg^{-1} for the silt and clay size fractions. Below 25 cm, N concentrations are not substantially different between the individual silt and clay particle size separates. For instance, at a depth of 25-50 cm, values only range from 2.23 g N kg^{-1} for the coarse silt fraction to 2.63 g N kg^{-1} for the fine clay fraction. Between 90 and 110 cm, values range from 1.15 g N kg^{-1} for fine clays to 1.48 g N kg^{-1} for fine silts.

Figure 4.14: N Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile as a Function of Depth

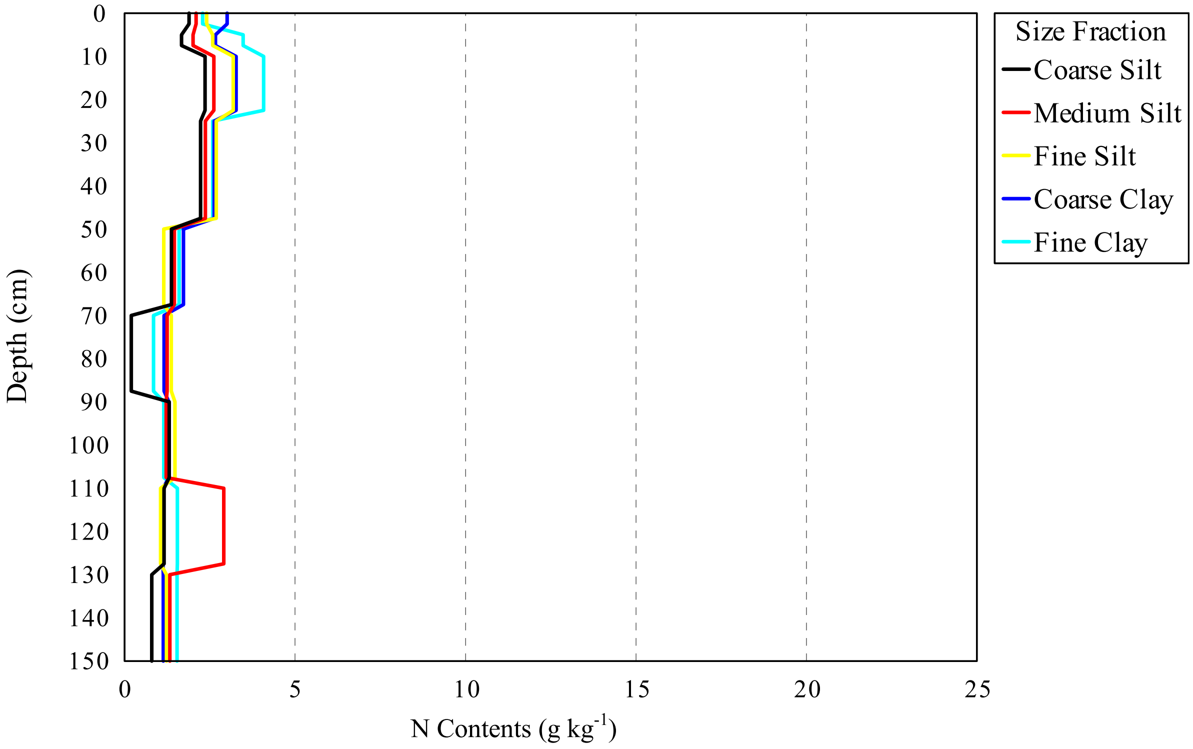
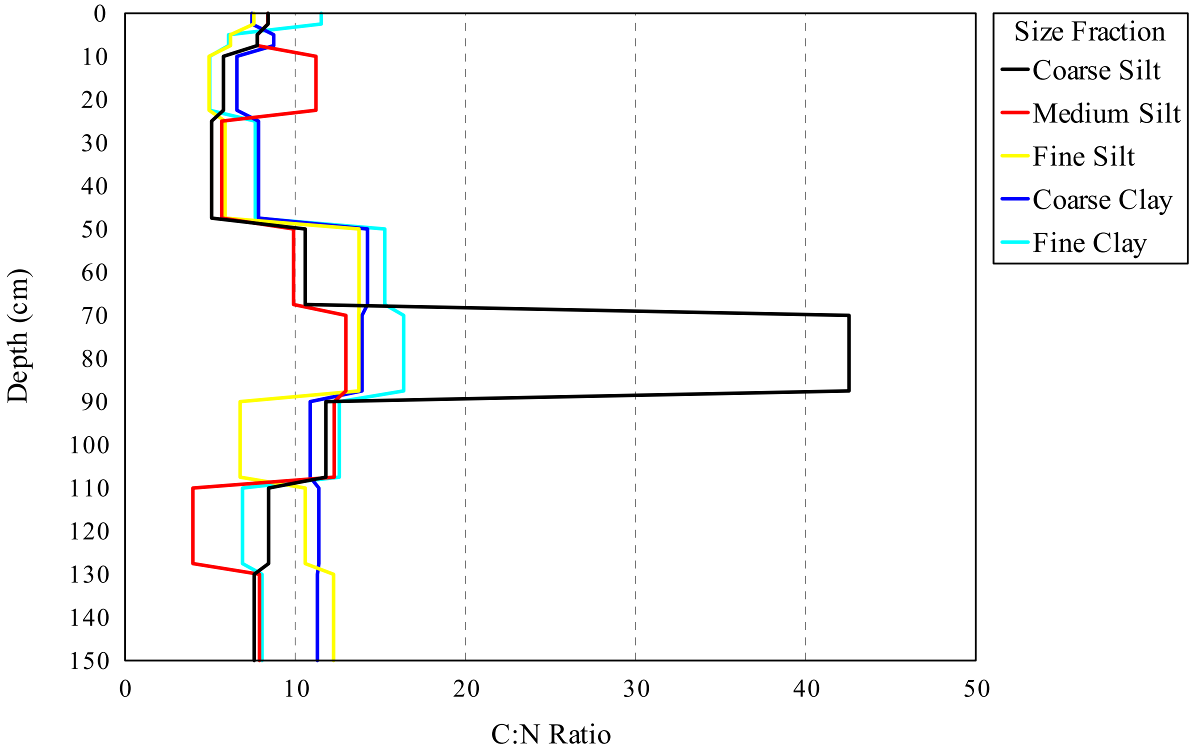


Figure 4.15: C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile as a Function of Depth

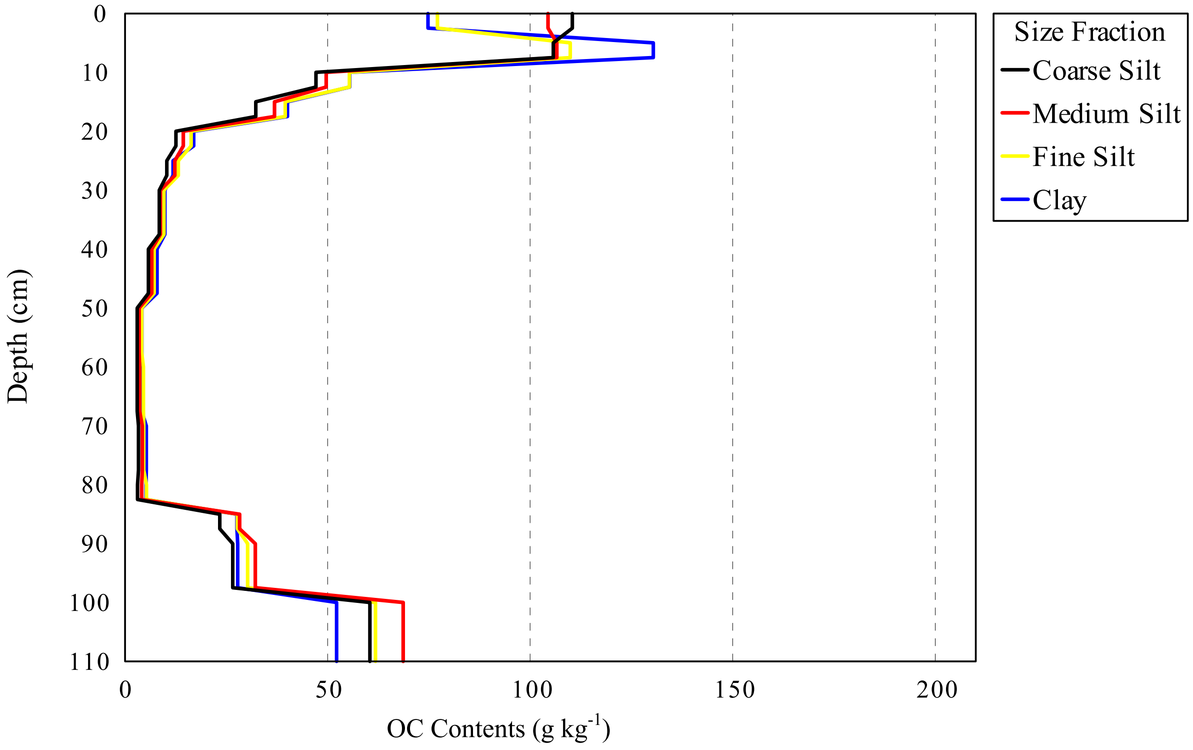


Most ratios of C:N for the particle size separates fall below 10 down to a profile of depth of 50 cm, reflective of the low organic inputs at this site. The ratio of C:N then increases, however, for all size separates (i.e. between 10 and 20 for most silts and clays). The C:N ratio is particularly high for the coarse silt fraction between 70 and 90 cm (i.e. >40), due to a significant reduction in N concentrations relative to OC. Below 90 cm, the ratio of C:N declines again for most size separates and depths.

4.1.6 Profile 5: Frankfurter Stadtwald

The OC and N contents and the ratios of C:N for the individual particle size fractions are displayed in Figures 4.16, 4.17 and 4.18, respectively. The results are given in Table C.14, Appendix C. Sand size fractions, as well as fine clay separates, were not measured in prior analyses of this profile. We can assume, however, that, similar to the other profiles, the silt and clay fractions contain significantly greater amounts of OC and N than the sand size separates. With the exception of samples from depths of 0-5, 25-30 and 85-110 cm, the greatest amount of OC is associated with fine silt and, especially, clay. For the coarse silt fractions, contents range from 110.40 g OC kg^{-1} for the top 5 cm to about 3 g OC kg^{-1} for samples from 50-85 cm. For the clay fractions, contents vary from 130.40 g OC kg^{-1} for 5-10 cm to about 4 to 5 g OC kg^{-1} for depths between 50 and 85 cm. Below a depth of 85 cm, the OC contents of all individual size fractions increase significantly. At these depths, medium silts contain the greatest amount of OC, varying from 28.29 g kg^{-1} to as much as 68.66 g kg^{-1} for 85-90 and 100-110 cm, respectively. The OC contents of whole soil samples do not increase at these depths, as shown in Figure 4.1, as the contribution of the silt and clay fractions in terms of the total particle size distribution is very small (see Table B.25, Appendix B). Specifically, only 3 to 7% of the whole soil at these depths is comprised of silts and clays, the rest being sand. For most sampled depths, the fine silt and clay size fractions also contain the most N. For clays, for instance, values range from 20.82 g N kg^{-1} to about 0.7 g kg^{-1} for 0-5 and 50-70 cm, respectively. As with OC, N concentrations decrease with depth down to 85 cm, where it then increases for all silt and clay size fractions. This indicates the presence of less degraded forms of organic matter at these depths. Although medium silts contain the greatest amount of OC at these depths, the greatest N concentrations are associated with the fine silt and clay fractions.

Figure 4.16: OC Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile as a Function of Depth



The ratio of C:N is greatest for the coarse silt fractions for most depths, while clays typically have the lowest ratios. For the coarse silt fraction, the C:N ratio ranges from 22 for 5-10 cm to a low of 5 for 30-40 cm. For the clay size fractions, the ratio of C:N lies below 10 for most depths, varying from a low of 4 for 0-5 cm to a high of 11 for 100-110 cm. At a depth of 85+ cm, there is a noticeable increase in the C:N ratio for all particle size fractions.

Figure 4.17: N Contents (g kg^{-1}) of the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile as a Function of Depth

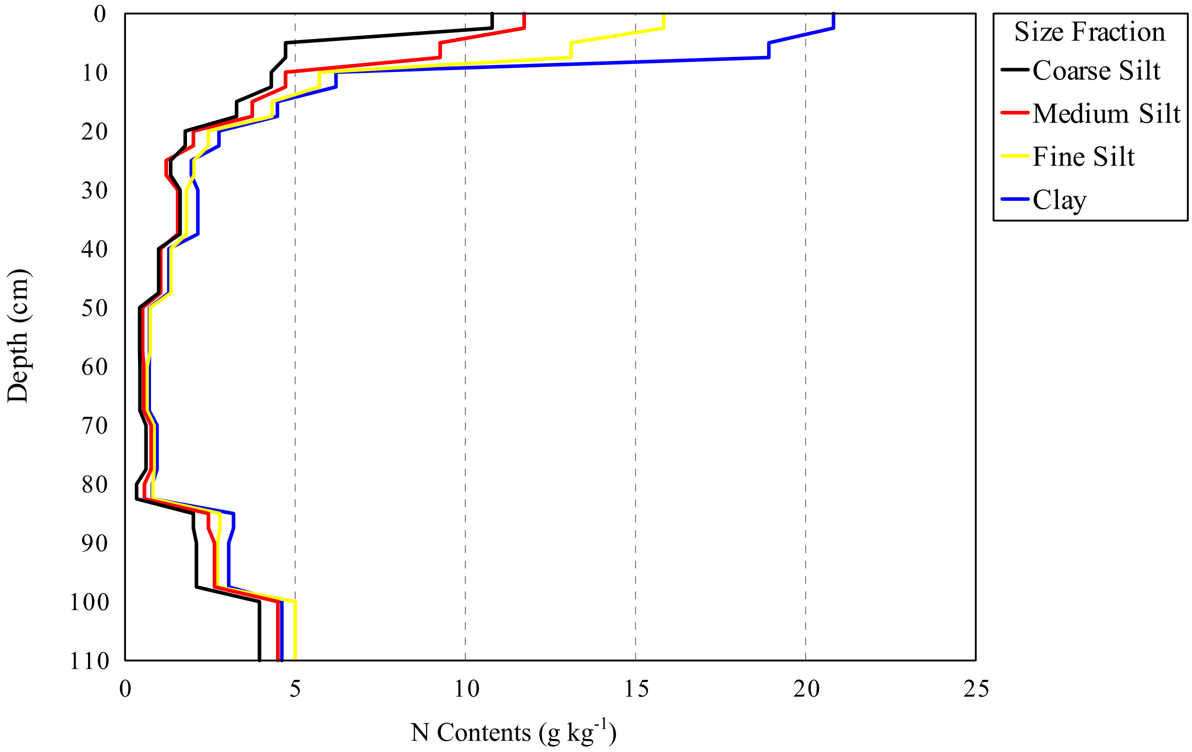
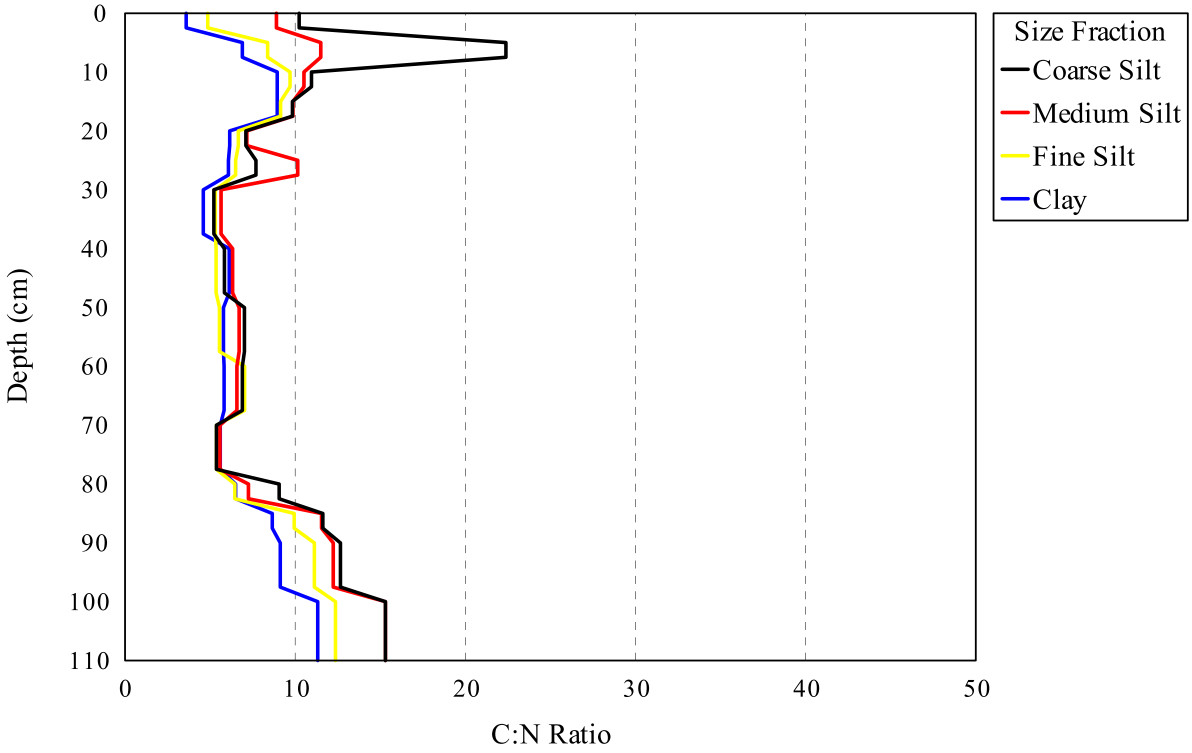


Figure 4.18: C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile as a Function of Depth



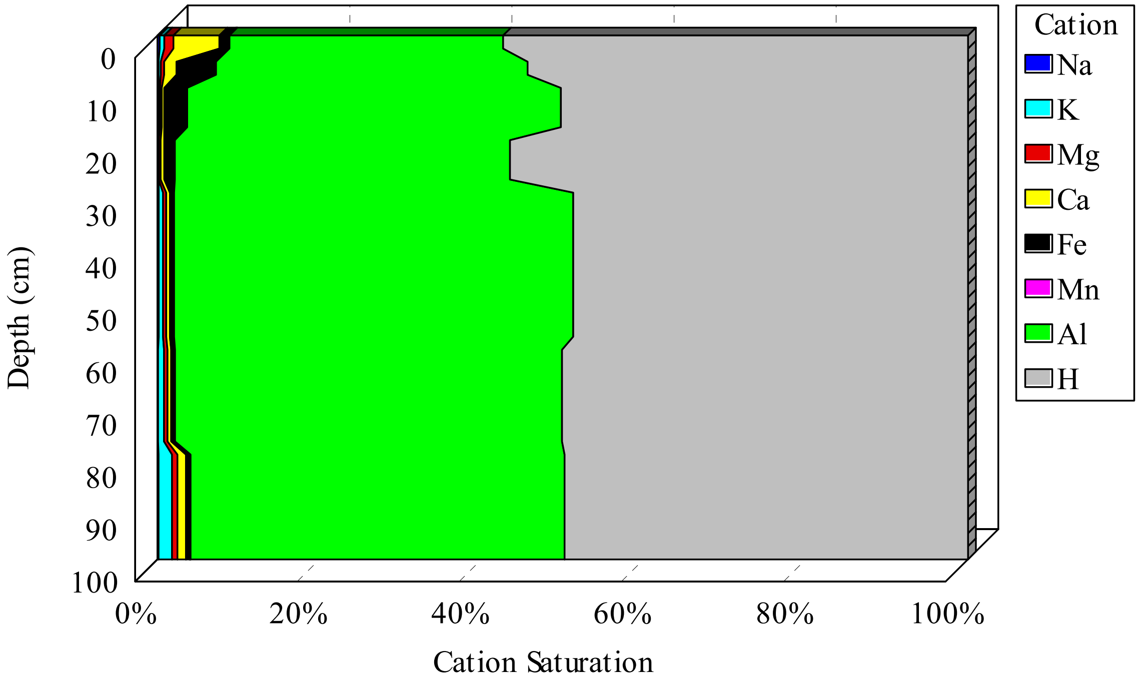
4.2 Potential Cation Exchange and Effective Cation Exchange Capacities and Cation Saturation

Potential Cation Exchange Capacity (CEC_{pot}) was analyzed for bulk soil samples (<2 mm) from the profiles Münden 1 and 2, Königstein and Geinsheim. Results for the Frankfurter Stadtwald profile were unfortunately not available. Effective Cation Exchange capacity (CEC_{eff}) was investigated for the profiles Münden 1 and 2 and Königstein, as this parameter is only measured for acidic soils.

4.2.1 Profile 1: Münden 1

Results for the CEC_{pot} and CEC_{eff}, together with the respective cations measured for bulk Münden 1 samples, are given in Tables D.1 and D.2, Appendix D. The calculated percent saturation of the individual exchangeable cations is displayed in Figure 4.19. Readers are referred to Table D.3, Appendix D for the raw results. The CEC_{pot} decreases quite rapidly with profile depth, from 61.70 $cmol_c\ kg^{-1}$ for the top 5 cm to 7.42 $cmol_c\ kg^{-1}$ for 80-100+ cm. The CEC_{eff} does not decline as rapidly, varying from 29.55 $cmol_c\ kg^{-1}$ for the top 5 cm to 19.30 $cmol_c\ kg^{-1}$ for samples at depths of 10-20 cm. Below 20 cm, the CEC_{eff} remains rather stable, ranging between 12.03 and 13.41 $cmol_c\ kg^{-1}$. Clearly, the exchangeable base cations, Na, K, Ca and Mg are present in comparatively small quantities. Of these cations, Ca contributes most to the CEC_{pot} of the soil, particularly in the top 10 cm of the profile (e.g. 5.69% for 0-5 cm). Below a depth of 10 cm, Ca amounts decline to about 1% or less. Overall, Al and H ions are the most dominant in this profile, which is typical for acidic soils. H ions occur in the largest amounts, ranging from 57.35 to 48.70%. Values for Al range from 33.77% for the top 5 cm sampled to a maximum of 49.25% for 30-60 cm. Small amounts of exchangeable Fe are present, particularly in the top 20 cm of the profile, with a maximum of 4.77% at 5-10 cm. Na, K, Mg and Mn cations are comparatively unimportant.

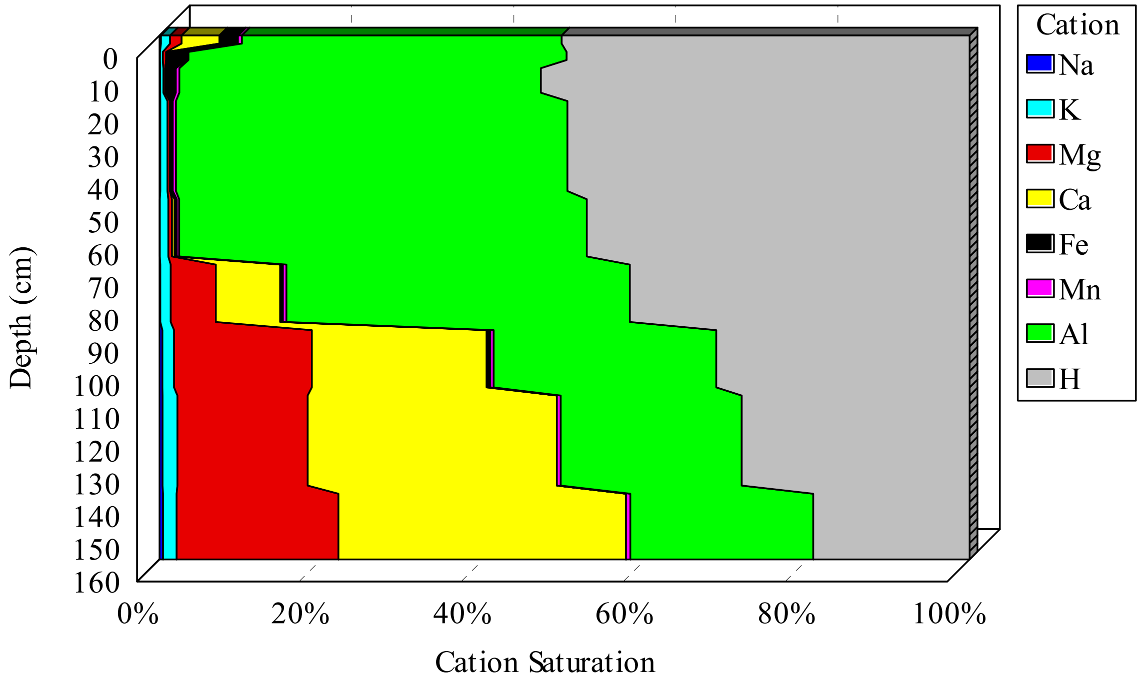
Figure 4.19: Percent Cation Saturation of Bulk Samples (<2 mm) from the Münden 1 Profile as a Function of Depth



4.2.2 Profile 2: Münden 2

For a detailed overview of the CEC_{pot} and CEC_{eff} for bulk soils for the Münden 2 profile, readers are referred to Tables D.4, D.5 and D.6, Appendix D. The calculated percent saturation of the respective exchangeable cations is shown in Figure 4.20. The CEC_{pot} for the top 10 cm of this profile is lower than that for Münden 1, with 41.06 $cmol_c\ kg^{-1}$ for 0-5 cm and 13.13 $cmol_c\ kg^{-1}$ for 5-10 cm. Below a depth of 10 cm, the CEC_{pot} remains rather stable, ranging between 10.58 and 13.88 $cmol_c\ kg^{-1}$ to the bottom of the profile. The CEC_{eff} is much lower for the top 5 cm of the profile, with 28.12 $cmol_c\ kg^{-1}$. Between 10 and 20 cm, the CEC_{eff} declines to 12.44 $cmol_c\ kg^{-1}$. This then increases somewhat to a depth of 90-110 cm, where a CEC_{eff} of 22.50 $cmol_c\ kg^{-1}$ was measured. At lower depths, CEC_{eff} declines, reaching a profile low of 9.83 $cmol_c\ kg^{-1}$ for the IIilCv horizon (i.e. 140 to 160+ cm).

Figure 4.20: Percent Cation Saturation of Bulk Samples (<2 mm) from the Münden 2 Profile as a Function of Depth



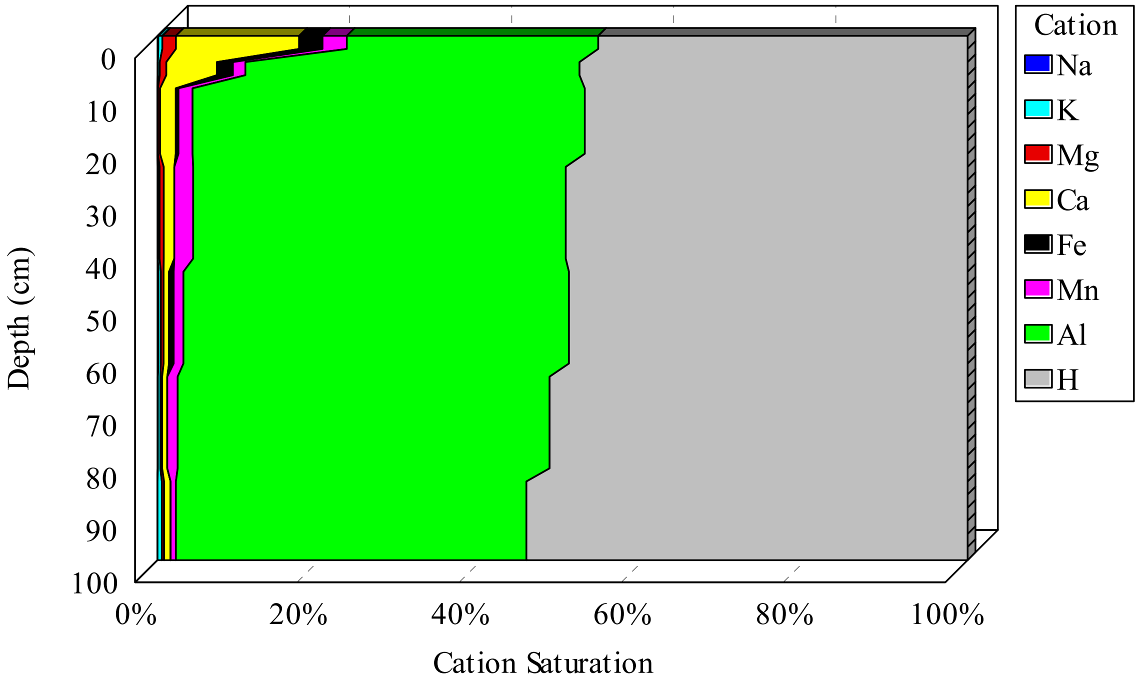
Similar to the profile Münden 1, H and Al are the most prevalent exchangeable cations. At lower depths, however, their relative amounts decline. Proportions of H range from a profile maximum of 52.94% for 10-20 cm to a low of 19.30% for the lowest sampled depth of 140-160+ cm. The greatest amounts of Al are found down to a depth of about 90 cm, with 39.46% for the upper 5 cm and 42.40% and 70-90 cm. At lower profile depths, particularly below 90 cm, Ca becomes an important exchangeable cation, with a 21.57 and 35.51% saturation for 90-110 and 140-160+ cm, respectively. Mg also occurs in rather large amounts at these depths (i.e. between 16.10 and 19.95%). Fe is primarily present in the top layers of this profile, with 2.29% for 0-5 cm. This proportional amount of this exchangeable cation falls below 1% at depths lower than 20 cm. K varies from 0.35 (i.e. 5-10 cm) to 1.83% (i.e. 110-140 cm) in this profile. Exchangeable Na and Mn are comparatively insignificant in terms of their contribution to the CEC of this profile.

4.2.3 Profile 3: Königstein

Of all four profiles, Königstein exhibits the greatest cation exchange capacity for the top 20 cm of the profile (see Tables D.7 and D.8, Appendix D). CEC_{pot} ranges from 69.98 $cmol_c\ kg^{-1}$ for the upper 5 cm sampled to 19.86 $cmol_c\ kg^{-1}$ for 10-25 cm. At depths of 25-85 cm, CEC_{pot}

is rather stable (i.e. 9.63 to 10.19 cmol$_c$ kg^{-1}). CEC$_{pot}$ reaches a profile low of 7.61 cmol$_c$ kg^{-1} for between 85 and 100+ cm. For the top 10 cm of this profile, CEC$_{eff}$ varies between 42.99 and 34.99 cmol$_c$ kg^{-1}. This then declines progressively throughout the profile to a low of 7.70 cmol$_c$ kg^{-1} for depths of 85-100+ cm.

Figure 4.21: Percent Cation Saturation of Bulk Samples (<2 mm) from the Königstein Profile as a Function of Depth

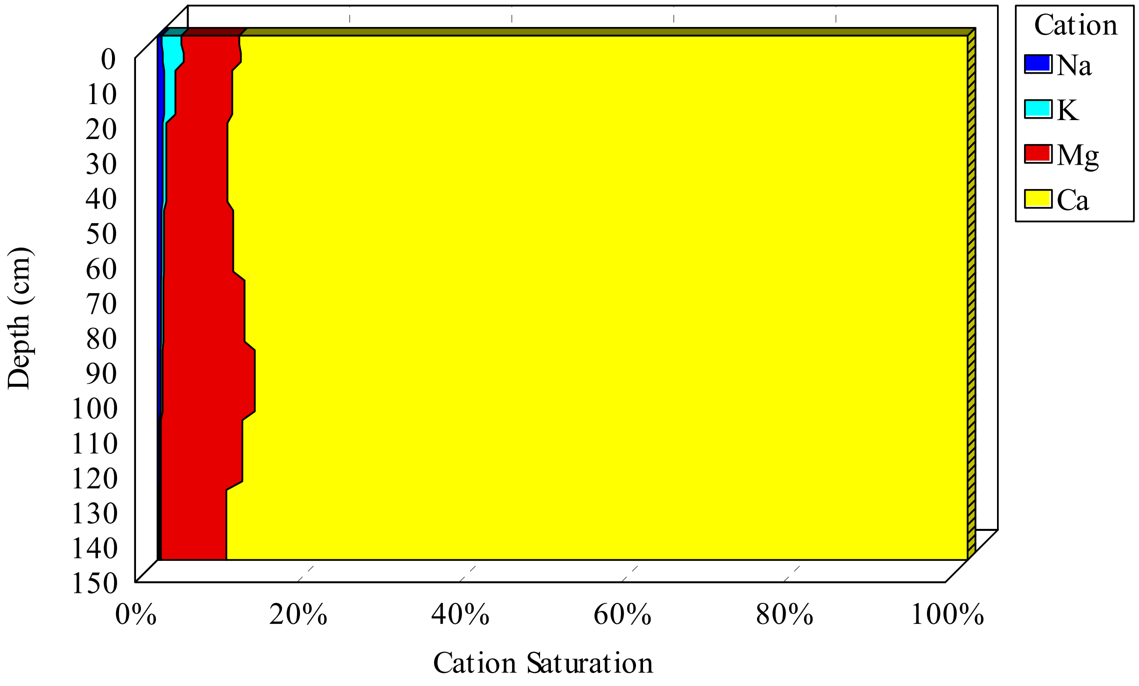


As shown in Figure 4.21, the base cations are rather insignificant in terms of the CEC of this profile, as is expected for acidic soils (see Table D.9, Appendix D for the raw data). Exchangeable Ca is, however, present in relatively significant quantities in the upper 10 cm of the profile, with saturation values of 15.22 and 6.23% for 0-5 and 5-10 cm, respectively. Similar to the Münden 1 and 2 profiles, exchangeable H and Al are the most important cations. For H, percentage amounts increase with depth, from 45.58 (i.e. 0-5 cm) to 54.46% (i.e. 80-100+ cm). Al ranges from 31.04 to a maximum of 47.59% for the depths of 0-5 and 30-60 cm, respectively. Mn occurs in greater amounts relative to the other profiles, varying from 3.00 (i.e. 0-5 cm) to 0.66% (80-100+ cm). Fe is primarily present in the top 10 cm of the soil (i.e. 2.87 to 1.99%), disappearing at lower depths. The proportional amount of Mg is rather small, with 1.68% at 0-5 cm and 0.27% at depths of 80-100+ cm. Na and K are relatively insignificant in terms of their contribution to the cation exchange capacity of this soil.

4.2.4 Profile 4: Geinsheim

The results for the CEC_{pot} and percent cation saturation of the Geinsheim profile are shown in Tables D.10 and D.11, Appendix D. The top layers of this soil profile have the lowest CEC_{pot} compared to the other soils investigated. Values range from 34.66 to 30.88 $cmol_c\ kg^{-1}$ for the top 25 cm sampled. The CEC_{pot} in the M and IIP horizons (i.e. 25-90 cm) then increases significantly to between 40.24 and 47.10 $cmol_c\ kg^{-1}$, which is higher than that measured for comparable depths for the other profiles. At depths where the relict Chernozem occurs (i.e. below 90 cm), CEC_{pot} then declines from 35.78 $cmol_c\ kg^{-1}$ (i.e. 90-110 cm) to 20.54 $cmol_c\ kg^{-1}$ (i.e. 110-130 cm). At the lowest profile depth, where the sand size fraction dominates (i.e. 130-150+ cm), the CEC_{pot} reaches a profile low of 10.22 $cmol_c\ kg^{-1}$. Overall, the CEC_{pot} of this soil is rather small considering the amount of smectites in this profile, minerals which have a CEC that ranges from 70 to 130 $cmol_c\ kg^{-1}$ (AG Boden 1994).

Figure 4.22: Percent Cation Saturation of Bulk Samples (<2 mm) from the Geinsheim Profile as a Function of Depth



As shown in Figure 4.22, Ca is the most prevalent exchangeable cation in this soil. Proportional amounts for Ca vary from about 89 to 91% for the entire sampled depth. Mg is quantitatively less important, with values that vary between 7.02 and 11.39%. K is present in relatively minor amounts, primarily occurring in the top 25 of the profile (i.e. 2.44 to 1.38%).

The exchangeable cation Na occurs in amounts of <1% for all profile depths. Given the alkalinity of this soil profile, exchangeable acid cations are not present in this profile (i.e. H-value = 0 (see Table D.10, Appendix D)).

4.3 X-ray Diffraction Results

Data regarding the first-order x-ray reflections for the identified clay minerals present in the respective soil profiles investigated are given in Tables E.1 to E.10, Appendix E. Where smectite was detected, the d-spacing values are given for the first-order (i.e. 001) reflection in both its air-dried and glycolated state. Vermiculite is often difficult to identify, especially if chlorite is also present, as their first-order reflections overlap (i.e. 6.09-6.22° 2θ and 6.18-6.31° 2θ, respectively). As such, values for the relative amount of vermiculite present in samples are inevitably overestimated as it includes some chlorite. The chlorite amounts were calculated from the 7.1 Å peak. This peak also overlaps with another mineral, kaolinite, but is more easily isolated and the area determined for quantitative purposes. The relative amount of kaolinite in samples is also estimated from the area of the 7.1 Å peak. Mixed layered minerals of both illite and smectite, which have a d-spacing which falls in the range of 11 to 12 Å are perhaps the most common minerals found in soils as illite forms from smectite (Moore and Reynolds 1997). Such minerals are, thus, not surprisingly present in almost every sample analyzed. The relative percent of illite was calculated from the 10 Å reflection. Values of FWHM (i.e. full width at half the maximum value) are particularly informative for illite, providing a good indication of the crystallinity and purity of this mineral. The quantitative estimates for the mineral composition of the clay size fractions (i.e. <2 μm) are presented in Tables E.6 to E.10. The relative amounts of non-clay minerals, notably quartz, k-feldspars, albite and goethite, are also given. A selected number of the >80 diffraction patterns conducted for all of the profiles are shown in Appendix F.

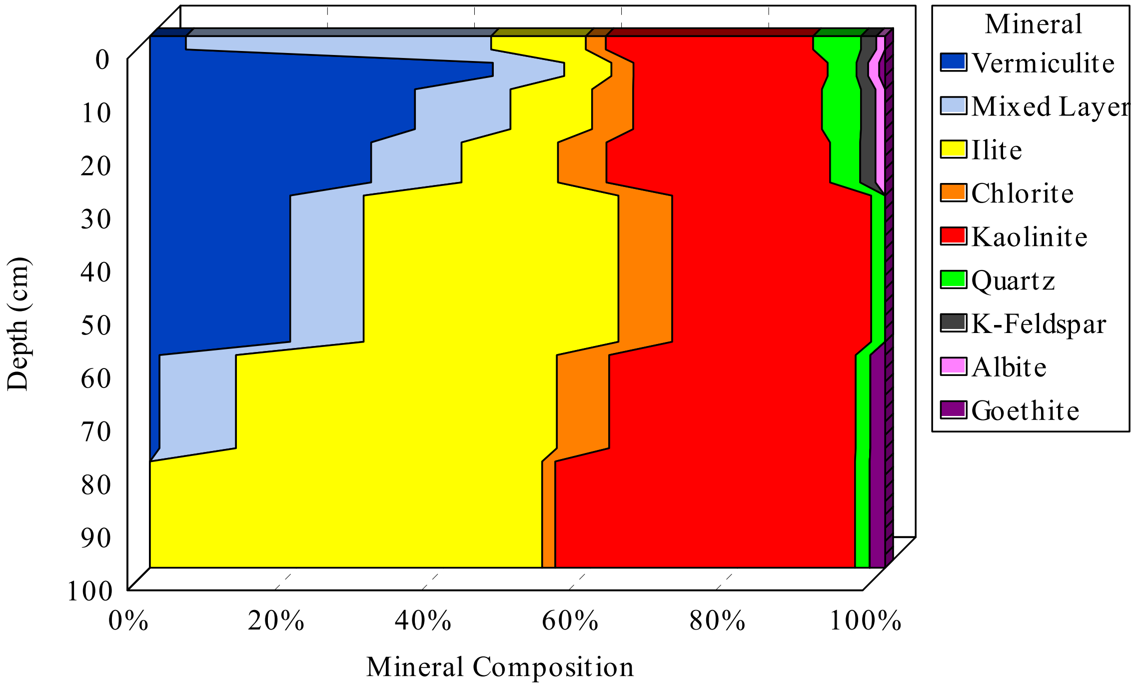
Quantitative estimates regarding the mineral composition of the clay size fractions for each profile, which are presented below in graphical form, are to be interpreted as relative and not absolute amounts. As the quantitative determination of clay minerals is very difficult, one must exercise caution in the interpretation of results. As stated by Moore and Reynolds (1997; 227), "…quantitative analysis may be more of an art than a science."

4.3.1 Profile 1: Münden 1

Clay minerals identified in the <2 µm fractions separated from whole soil samples of the Münden 1 profile include vermiculite, mixed layered minerals (i.e. smectite/illite), chlorite, illite and kaolinite (see Figure 4.23). Smectite is not present, as indicated by the absence of a 16 to 17 Å reflection in the glycolated state. Vermiculite varies quite substantially according to depth. While only an approximate 5% of vermiculite was found to be present in the top 5 cm, this increased significantly to between 47% and 30% from depths of 5-30 cm. Below 30 cm, vermiculite decreases rapidly and is non-existent at a depth of greater than 80 cm. The amount of mixed layered minerals, the presence of which is indicated by a low-angle shoulder on the 001 chlorite/vermiculite reflection (i.e. ca. 14 Å), appears highest in the top 5 cm (i.e. about 42%). Amounts then decline to about 10% at lower depths, where its presence in relational terms remains rather stable. Mixed layer minerals are absent at depths of 80-100+ cm. The opposite pattern is observed for illite. Specifically, illite significantly increases with depth in this profile, from about 13% in the top 5 cm to 53% at depths of 80-100+ cm. This is a pattern that is often observed for soils, as burial processes often cause a transition of smectite to illite (Moore and Reynolds 1997). Illite can also turn into smectite, a process instigated by weathering. Chlorite occurs in relatively small amounts, ranging from about 3% in the top 10 cm to slightly over 7% between 30 and 80 cm. Kaolinite is present in significant amounts at all depths, varying between 25 and 41% throughout the profile.

Quartz is also present in this fraction at all depths (i.e. about 2 to 7%), while k-feldspars and albite were only detected down to a depth of 30 cm (i.e. between 1 and 2% for both minerals). Goethite is virtually absent at most depths, appearing in measurable amounts at depths of greater than 80 cm (i.e. ca. 2%).

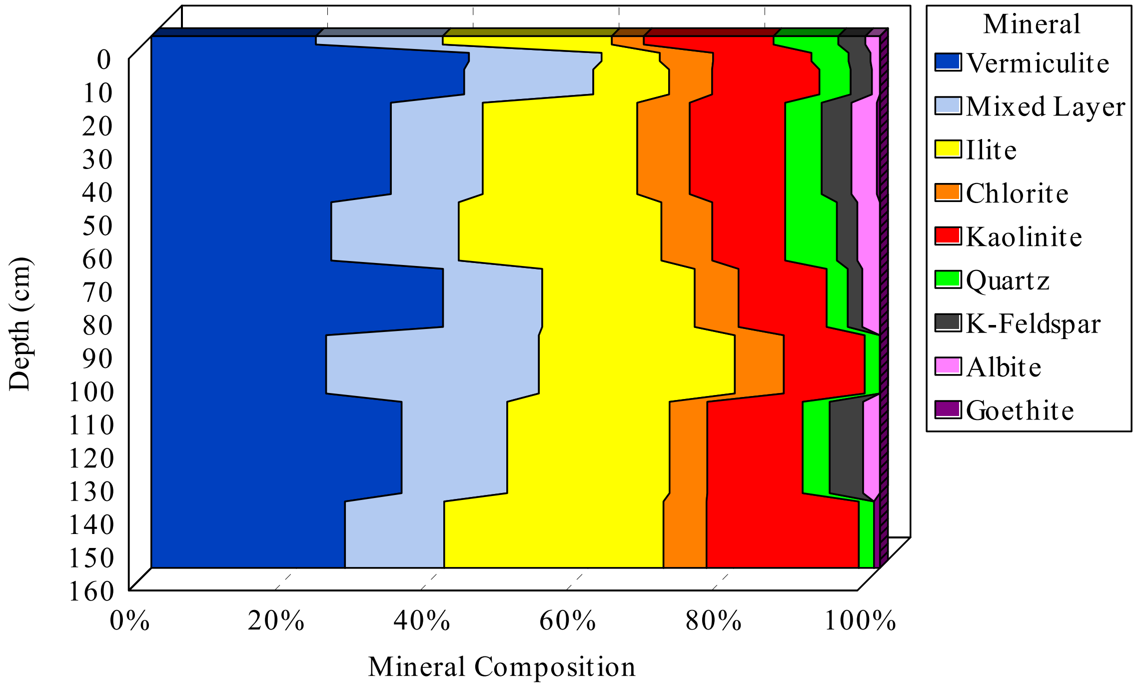
Figure 4.23: Mineral Composition of the Clay Mineral Fraction (<2 µm) from the Münden 1 Profile as a Function of Depth



4.3.2 Profile 2: Münden 2

The profile Münden 2 displays a similar clay mineral composition as does Münden 1, with a dominance of vermiculite, mixed layered minerals, illite and kaolinite (see Figure 4.24). Vermiculite occurs in the greatest amounts between 5 and 20 cm (i.e. around 43%) and then generally declines with depth, albeit not to the same extent. Contents do not fall below about 24% in this profile. Mixed layer mineral amounts are variable with depth, ranging from profile low of about 13% (i.e. 20-50 cm) to a high of 29% (i.e. 90-110 cm). With the exception of depths at 5-20 cm, the quantity of illite ranges between about 20 and 30% at all profile depths. The relative amount of kaolinite varies from 10 to 20% throughout the profile. Chlorite is of lesser importance in this profile in terms of its quantity, ranging between an approximate 4 and 7%.

Figure 4.24: Mineral Composition of the Clay Mineral Fraction (<2 µm) from the Münden 2 Profile as a Function of Depth



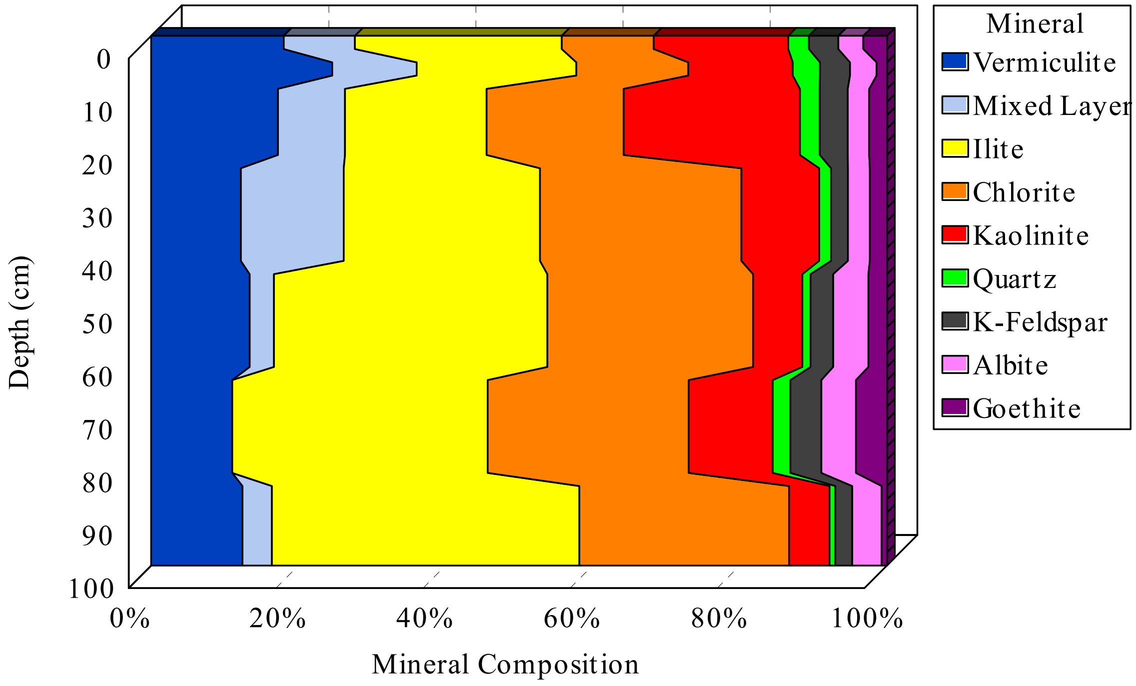
Non-clay minerals present in the clay size fraction include quartz (i.e. 2 to 9%), k-feldspars (i.e. 0 to 4%) and albite (i.e. 0 to 4%). Goethite is virtually non-existent but was detectable in two samples (i.e. 20-50 cm and 140-160+ cm).

4.3.3 Profile 3: Königstein

Similar to Münden 1 and 2, vermiculite, chlorite, illite and kaolinite dominate the clay mineral fraction of samples from Königstein (see Figure 4.25). Initial suspicions that smectite may be present in this profile proved to be unfounded. The low angle bulge present on the shoulder of rather broad reflections occurring about the 14 Å for air-dried samples down to a depth of about 25 cm was unaffected by treatment with ethylene glycol, a strong indication of the presence of vermiculite and not smectite. This low-angle bulge can be nicely seen in Figure F.5, Appendix F, which presents the diffraction pattern for the sample from 0-5 cm. At these depths, vermiculite amounts to about 17 to 25%, declining to around 12% for depths below 25 cm. Mixed layered minerals are present in relatively small amounts, with values ranging from 0 (i.e. 65-85 cm) to 14% (i.e. 25-45 cm). Illite is perhaps the most significant clay mineral present in this profile. With a couple of exceptions, the quantity of illite generally increases with depth, reaching a high of over 40% at a depth of 85-100+ cm. At these low depths, the illite reflections and estimates for FWHM (i.e. <0.3) suggest the presence of an illite form which is highly crystalline and which has been subject to very high temperatures at some point (see Figure F.6, Appendix F for an example). Chlorite is present in greater quantities at this site compared to the profiles, increasing with depth from a virtual 13% for the top 5 cm to about 29% for 85-100+ cm. Kaolinite ranges in amounts of about 24 (i.e. 10-25 cm) to 6% (i.e. 85-100+ cm).

Quartz is also present, varying from about 1 (i.e. 85-100+ cm) to 4% (i.e. 5-10 cm). K-feldspars (i.e. 2 to 4%), albite (i.e. 3 to 5%) and goethite (i.e. 1 to 4%) appear in measurable quantities at all depths.

Figure 4.25: Mineral Composition of the Clay Mineral Fraction (<2 µm) from the Königstein Profile as a Function of Depth

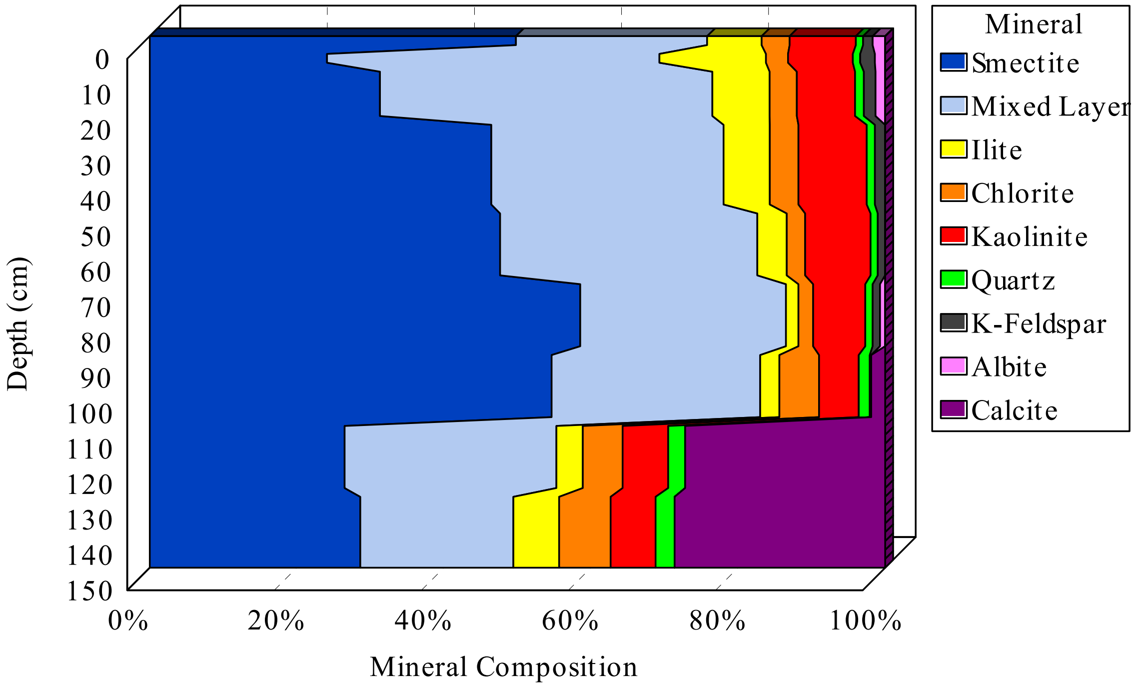


4.3.4 Profile 4: Geinsheim

In opposition to the preceding soils discussed, the Geinsheim profile contains significant amounts of smectites (se Figure 4.26). For depths of 0-5 cm and 25-110 cm, smectites occur in amounts of about 47 to 59%. The sample taken from a depth of 5-10 cm had an estimated amount of only 24% and, thus, appears to be an anomaly due to either poor sample preparation or inhomogeneity. At depths below 110 cm, smectite amounts decline to about 27 to 29%. For the majority of samples analysed, solvation with ethylene glycol did not result in a predicted 17 Å first-order reflection. This could have been the result of suboptimal solvation conditions. This is less likely, however, as care was taken to ensure that samples were exposed to the ethylene glycol long enough for the minerals to take up two monolayers of this organic compound (i.e. a minimum of two days). Many samples were also exposed to ethylene glycol repeatedly to ensure minerals had swelled to their maximum. This suboptimal expansion of smectites was more likely due to the minerals themselves, which unfortunately do not always expand to 17 Å upon solvation (Moore and Reynolds 1997), or the interference of mixed layered minerals in the analysis of x-ray reflections.

The presence of large amounts of mixed layer minerals at all depths in the Geinsheim profile, which varied from a profile high of 45 (i.e. 5-25 cm) to a low of 21% (i.e. 140-160 cm), made it somewhat difficult to determine the exact peak occurrence of smectites. Illite and chlorite are present in comparatively small quantities, with amounts ranging from 15 (i.e. 5-10 cm) to 2% (i.e. 70-90 cm) and 7 (i.e. 140-160+ cm) and 2% (i.e. 70-90 cm), respectively. Kaolinite appears in amounts of between 5 and 10% for all depths.

Figure 4.26: Mineral Composition of the Clay Mineral Fraction (<2 µm) from the Geinsheim Profile as a Function of Depth



The results of the Greene-Kelly test, which allows for a determination of smectite mineral type (see MacEwan and Wilson 1980; Moore and Reynolds 1997), were not completely conclusive due to the interference of interlayer complexes with illite but indicated the presence of montmorillonite.

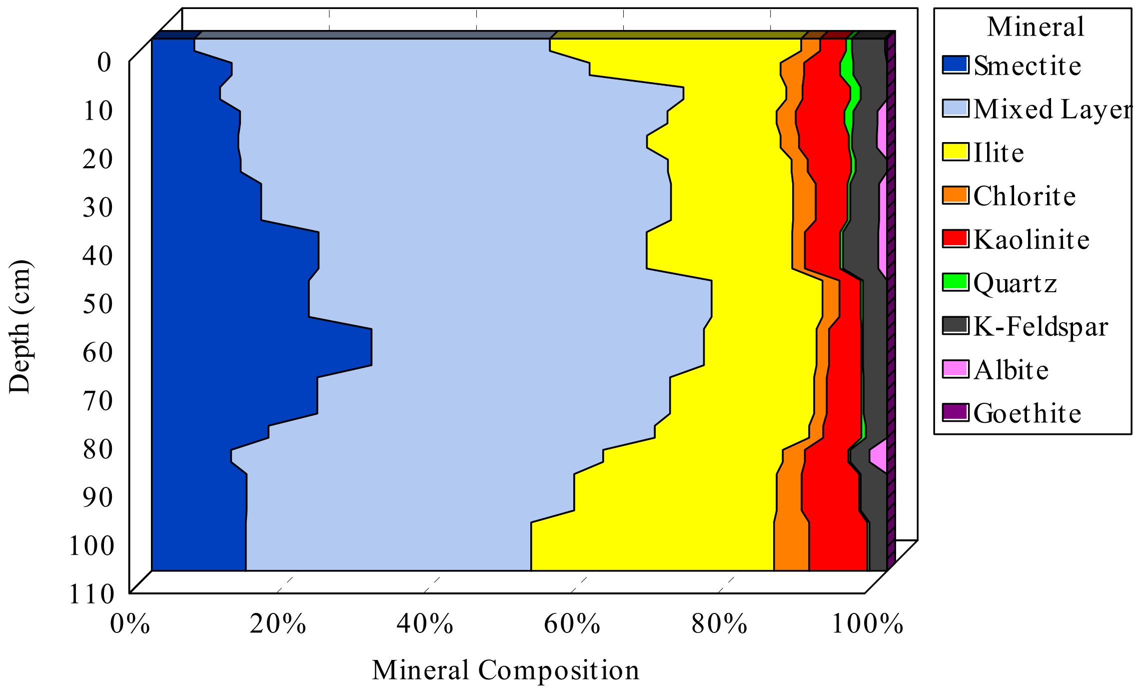
4.3.5 Profile 5: Frankfurter Stadtwald

Similar to the Geinsheim profile, the Frankfurter Stadtwald site contains smectites, mixed layered minerals, illite, chlorite and kaolinite (see Figure 4.27). Smectites are present in lesser quantities, however, the amounts of which generally increase with depth down to about 70 cm (i.e. from 6% for 0-5 cm to 30% for 60-70 cm). Below this, smectites decrease in relative terms, ranging from about 11 to 13% between 85 and 110 cm. Most smectite minerals in samples swelled to an approximate 17 Å after solvation with ethylene glycol. Mixed layered minerals dominate the clay composition of this profile, varying in quantities of about 63 (i.e. 10-15 cm) to 39% (i.e. 100-110 cm). Given this, we could assume that the transition of smectite to illite in this profile is more advanced compared to the Geinsheim profile. There is more illite present, with a high of 34% (i.e. 0-5 cm) and a low of 14% (i.e. 10-15 cm). Chlorite and kaolinite are present in comparatively low amounts (i.e. 2 to 5% and 3 to 8%, respectively).

Apart from clay minerals, quartz (i.e. 0.2 to 2%), k-feldspars (i.e. 2 to 5%) and some albite (i.e. 0 to 2%) were detected in samples. Goethite is virtually absent.

The results of the Greene-Kelly test performed on two of the samples indicate the presence of montmorillonite in this soil. Although the first-order smectite reflection did not completely collapse and produce a first-order spacing of 9.6 Å (i.e. a partial reflection remained at about 16.2 Å), likely due to the presence of interlayer complexing with illite, the intensity of the reflection declined significantly for both prepared samples. If another type of smectite were present, the first-order peak would have expanded and shifted to 17.7 Å (see MacEwan and Wilson 1980; Moore and Reynolds 1997).

Figure 4.27: Mineral Composition of the Clay Mineral Fraction (<2 µm) from the Frankfurter Stadtwald Profile as a Function of Depth



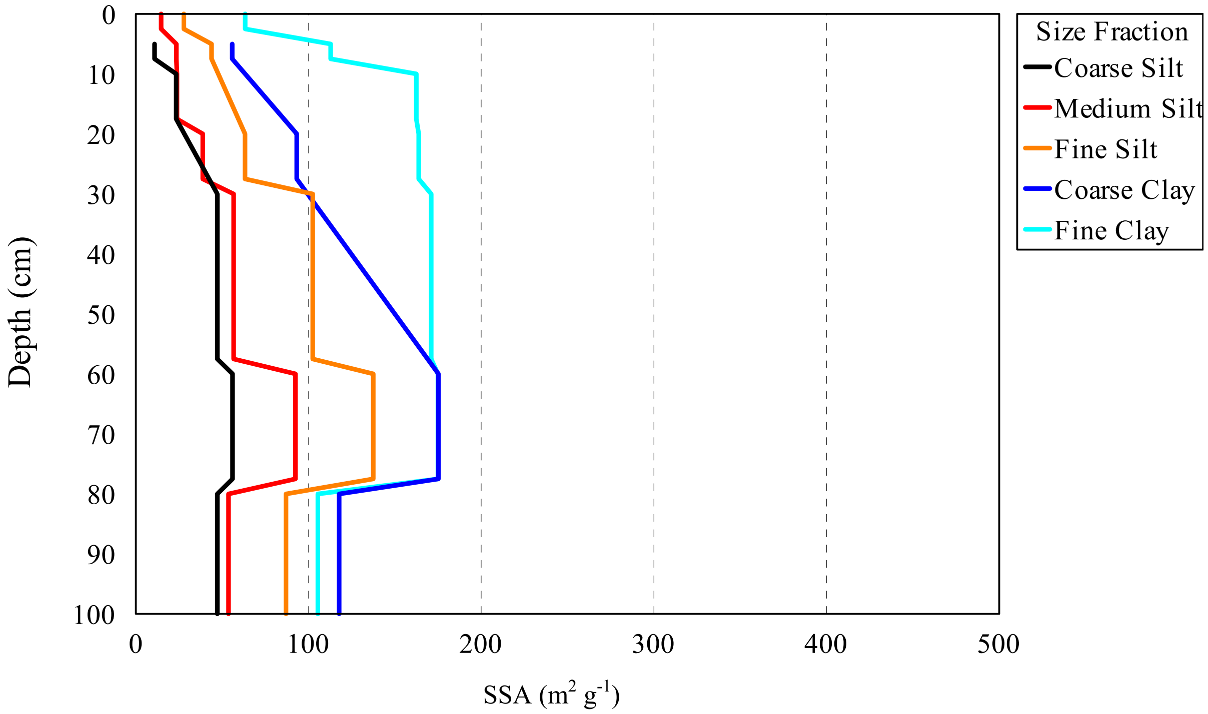
4.4 Specific Surface Area

Specific surface area (SSA) is fundamentally influenced by the mineral composition of a soil and the respective particle size fraction analysed. As the surface to volume ratio increases with progressively smaller particle size fractions, SSA is expected to increase in moving from the silt to the clay separates. In terms of mineral composition, the presence of smectites, vermiculite and oxides will enhance the SSA of a soil, while clay minerals such as kaolinite and illite will result in lower values. The results of the SSA analyses of the silt and clay fractions isolated from the soil profiles will be discussed below.

4.4.1 Profile 1: Münden 1

Figure 4.28 displays the SSA of the silt and clay size separates analyzed (see Table G.1, Appendix G for an overview of the raw data). SSA for the coarse size silts and clays start at a depth of 5 cm due to the absence of values for these separates from samples taken at 0-5 cm. Down to a depth of about 80 cm, SSA increases significantly with depth for all particle size separates. This is common for soils, as the SSA of individual particles increases with age and the effects of erosion (i.e. an increase in surface roughness). At a depth of 30-60 cm, the SSA for coarse and medium silts approaches or is greater than 50 m^2 g^{-1}, while fine silts and clays have SSAs of more than 100 m^2 g^{-1}. SSA peaks at a depth of 60-80 cm for all separates. For instance, fine silts and clays increase from 28 and 63 m^2 g^{-1} for the upper 5 cm of the profile to 138 and 175 m^2 g^{-1} for 60-80 cm, respectively. At the lowest sampled depths of 80-100+ cm, there is a decrease in the SSA of all size fractions. This is perhaps due to an enhanced crystallinity of the clay minerals found as these depths, and a corresponding decrease in surface roughness, as well as the absence of minerals with a higher SSA such as vermiculite.

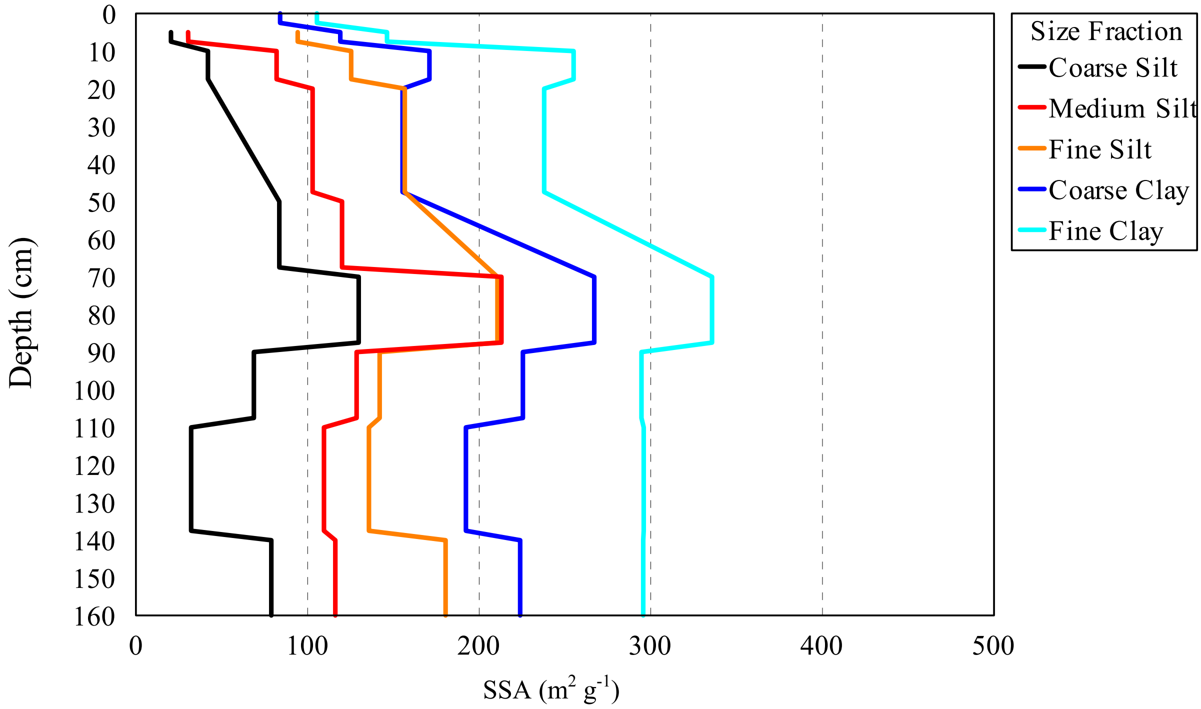
Figure 4.28: Specific Surface Area (m^2 g^{-1}) of the Silt and Clay Size Separates (<63 µm) from the Münden 1 Profile as a Function of Depth



4.4.2 Profile 2: Münden 2

As shown in Figure 4.29, the respective silt and clay size separates from Münden 2 have a greater SSA compared to Münden 1 (see Table G.2, Appendix G). SSA values for all silt separates are unfortunately missing for 0-5 cm. For samples from 5-10 cm, SSA for coarse silt is 20 m^2 g^{-1}, while fine clay has an area of 146 m^2 g^{-1}. The SSA for all size separates increases at lower depths and peaks at 70-90 cm, with values ranging from 130 to 336 m^2 g^{-1} for coarse silts and fine clays, respectively. These values are rather high and could be attributed to the presence of amorphous minerals at these depths or an increase in particle surface roughness. Below 90 cm, SSA declines somewhat for all separates.

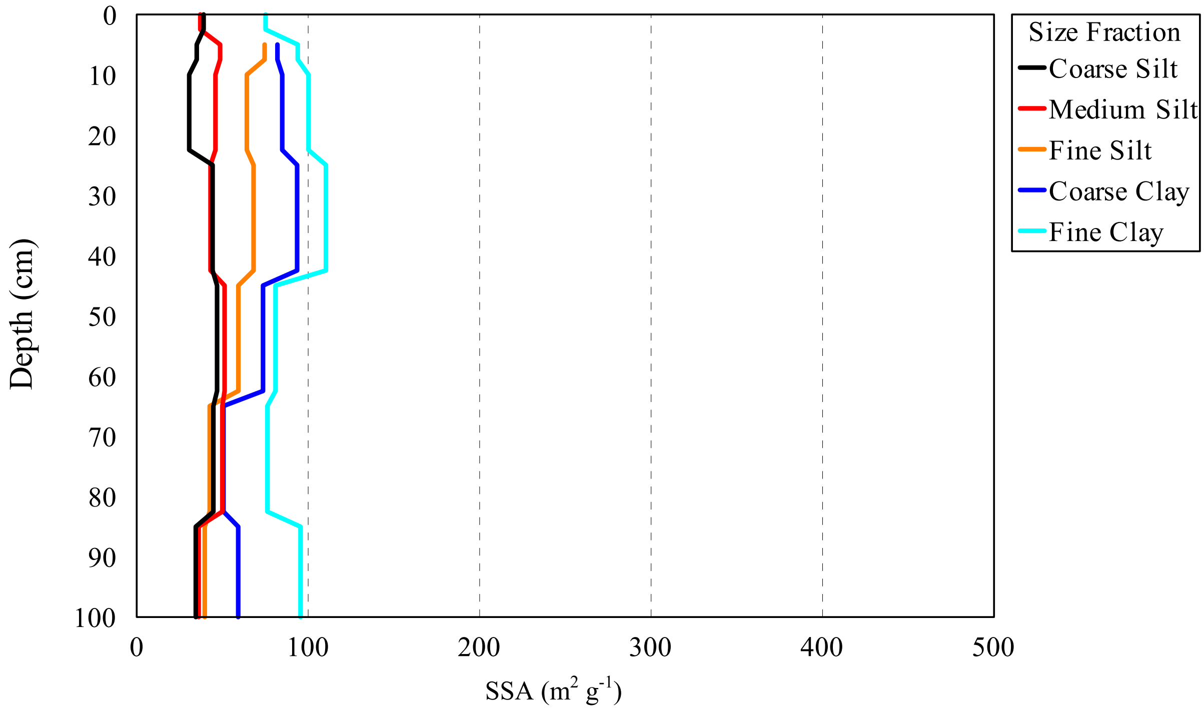
Figure 4.29: Specific Surface Area (m^2 g^{-1}) of the Silt and Clay Size Separates (<63 µm) from the Münden 2 Profile as a Function of Depth



4.4.3 Profile 3: Königstein

For an overview of the raw data for the Königstein profile, readers are referred to Table G.3, Appendix G. As displayed in Figure 4.30, variability in measured values for the individual size separates from Königstein is not as pronounced as with other profiles. Down to a depth of about 25 cm, values for the respective separates do not vary to any significant extent. Coarse silts have an SSA of between 30 and 40 m^2 g^{-1} at these depths, while fine clays have a SSA of between 75 and 100 m^2 g^{-1}. The SSA of some separates, notably clays, increases slightly below 25 cm, however, reaching a profile maximum at a depth of 25-45 cm. Coarse and fine clay separates have a SSA of 94 and 110 m^2 g^{-1} at this depth, respectively. Below 45 cm, SSA then declines, particularly for fine silts and clays. This decrease corresponds with a reduced quantity of amorphous oxides found in this profile, as will be discussed later, and increases in the crystallinity of clay minerals, notably illite. This trend continues at the lowest sampled depths of greater than 85 cm for the larger silt fractions, probably due to an enhanced amount of quartz present in samples.

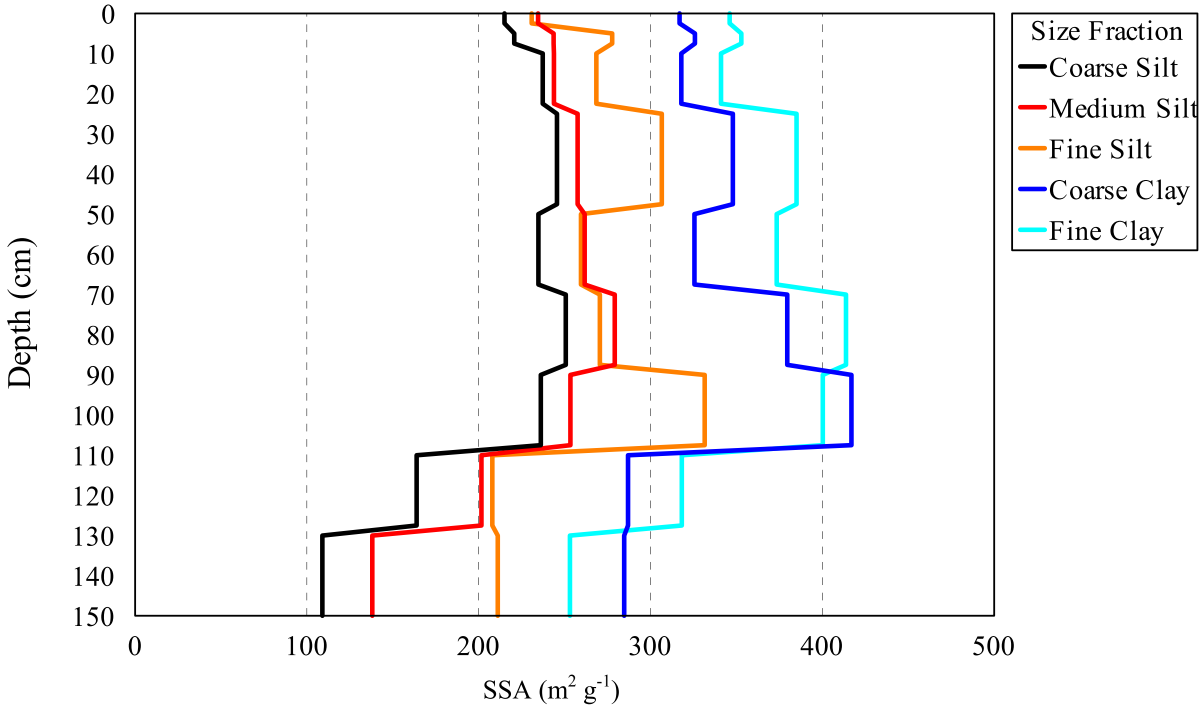
Figure 4.30: Specific Surface Area (m^2 g^{-1}) of the Silt and Clay Size Separates (<63 µm) from the Königstein Profile as a Function of Depth



4.4.4 Profile 4: Geinsheim

As shown in Figure 4.31, particle size separates from Geinsheim have a very large SSA, attributed to the high content of smectite minerals in this profile (see Table G.4, Appendix G for an overview of results). Smectite minerals have an SSA of as much as 800 m^2 g^{-1}, most of which is located in the interlayers of these minerals (Theng 1974; Kuntze et al. 1994). The coarser silt fractions also have relatively high SSAs, due to a certain amount of smectite minerals falling into these fractions as well. Given the high clay content of this soil and the fact that clay minerals strongly aggregate, an enhanced presence of clay size particles in the larger separates are an unavoidable effect. Although there is some variability in the respective SSAs of the individual particle fractions, values remain relatively stable, increasing slightly down to a depth of about 110 cm. For the coarse silt fraction, SSA ranges from 215 to 236 m^2 g^{-1} at depths of 0-110 cm. SSA for the fine clay fraction varies from 346 to 400 m^2 g^{-1} for these same depths. At lower depths (i.e. 110-150+ cm), where the amount of clay particles and smectite minerals significantly decline and the proportion of carbonates correspondingly increase, there is a decrease in SSA for all particle size fractions. At the lowest depths, coarse silt only has a SSA of 109 m^2 g^{-1}, while fine clays have a SSA of 253 m^2 g^{-1}.

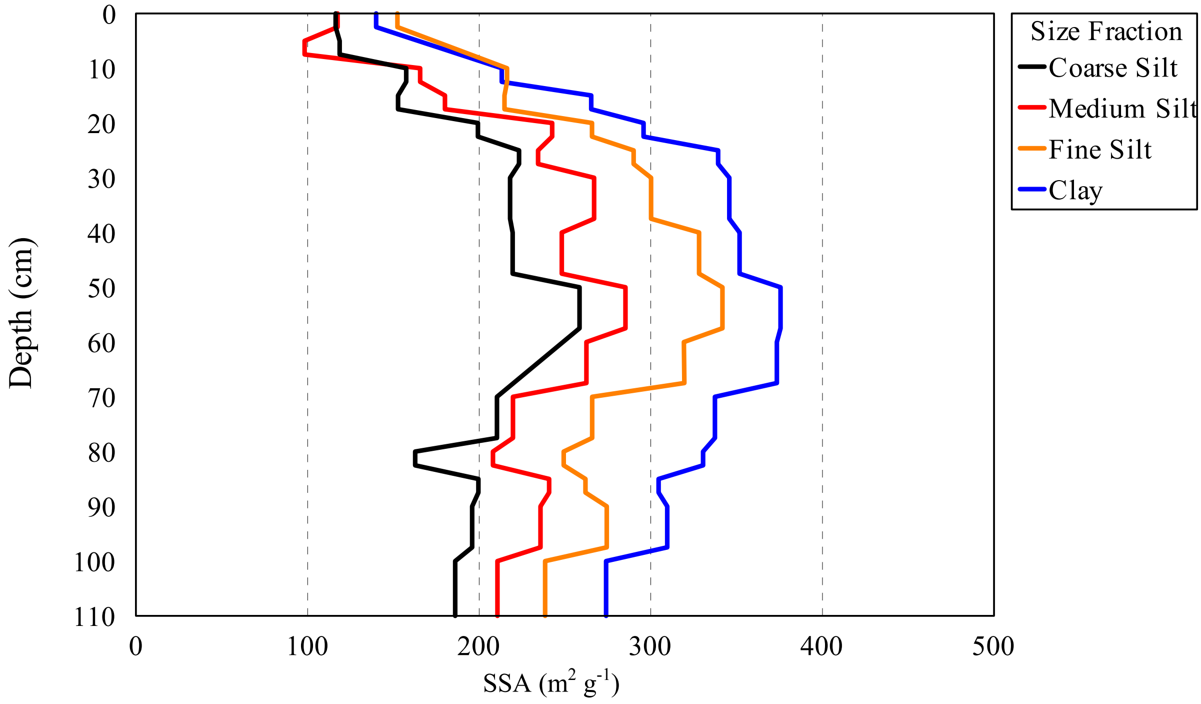
Figure 4.31: Specific Surface Area (m^2 g^{-1}) of the Silt and Clay Size Separates (<63 µm) from the Geinsheim Profile as a Function of Depth



4.4.5 Frankfurter Stadtwald

Figure 4.32 displays the SSA of the silt and clay size fractions from the Frankfurter Stadtwald profile. The raw data is given in Table G.5, Appendix G. Fine clay separates could not be analysed as with the other profiles, as only the <2 µm fraction had been separated from bulk samples in previous analyses of this profile. As with Geinsheim, the SSA of the individual size separates are high due to the presence of smectite minerals. The SSA of each size separate progressively increases down to about 70 cm. For instance, coarse size silts range from 116 m^2 g^{-1} for the top 5 cm to a high of 258 for a depth of 50-60 cm. Clays vary from 140 to 376 m^2 g^{-1} for the same depths, respectively. SSA generally decreases for all size separates from lower depths, corresponding with reduced quantities of smectites.

Figure 4.32: Specific Surface Area ($m^2\ g^{-1}$) of the Silt and Clay Size Separates (<63 µm) from the Frankfurter Stadtwald Profile as a Function of Depth



4.5 Specific Surface Area and Organic Carbon Loadings

OC loadings of mineral surfaces for the silt and clay size fractions were estimated to allow comparisons to be made to Mayer's (1994a) results and his proposed "monolayer equivalent" (ME). The importance of adsorptive processes in the preservation of soil organic matter can further be evaluated. As already discussed in the introduction, Mayer (1994a) defined a ME level of 0.86 mg OC m^{-2} using the results of 22 sediment cores from continental shelves of the North American continent. OC loadings of about 0.5 to 1.1 mg OC m^{-2} are in agreement with the ME zone (i.e. 95% confidence interval). Evidence has been provided which suggests that this level can also be applied to soils (Mayer 1994b). Estimated OC loadings for the fine particle size fractions for each profile are presented below.

4.5.1 Profile 1: Münden 1

As displayed in Table 4.1, OC loadings for the depth 0-10 cm are particularly high for most fractions (i.e. typically >2 mg OC m^{-2}). This is much greater than that predicted for a monolayer coverage of organic carbon on mineral surfaces and is clearly a result of the large organic matter inputs to the surface of the profile. At depths lower than 10 cm, loadings progressively drop to levels well below the ME zone. OC loadings are especially low at a depth of 30 cm and more, with values of 0.12 mg OC m^{-2} or less. The progressive declination of OC loadings throughout the profile suggests that sorptive processes of organic material onto mineral surfaces may not play a significant role in the stabilisation of OC in the Münden 1 profile.

Table 4.1: Calculated OC Loadings of the Silt and Clay Size Fractions (<63µm) from the Münden 1 Profile

Depth (cm)	**Horizon**	**Fraction**	**OC loading (mg m^{-2})**
0-5	Aeh	<63 µm	NA
		<20 µm	9.47
		<6.3 µm	5.98
		<2 µm	NA
		<1 µm	2.38
5-10	Ahe-Bv	<63 µm	3.32
		<20 µm	2.72
		<6.3 µm	2.61
		<2 µm	2.04
		<1 µm	0.90
10-20	Ah-Bv	<63 µm	1.05
		<20 µm	1.75
		<6.3 µm	NA
		<2 µm	NA
		<1 µm	0.37
20-30	Bv	<63 µm	NA
		<20 µm	0.45
		<6.3 µm	0.50
		<2 µm	0.38
		<1 µm	0.20
30-60	sBv	<63 µm	0.12
		<20 µm	0.12
		<6.3 µm	0.07
		<2 µm	NA
		<1 µm	0.08
60-80	IIBvCv	<63 µm	0.07
		<20 µm	0.10
		<6.3 µm	0.04
		<2 µm	0.04
		<1 µm	0.05
80-100+	IIiICv	<63 µm	0.05
		<20 µm	0.06
		<6.3 µm	0.04
		<2 µm	0.06
		<1 µm	0.09

4.5.2 Profile 2: Münden 2

As shown in Table 4.2, the silt and clay size fractions have relatively high OC loadings in the upper 5 cm of the Münden 2 profile. Loadings then rapidly decline below this depth to levels below that predicted for a monolayer coverage of organic carbon on mineral surfaces. OC loadings already fall below 0.20 mg OC m^{-2} at profile depths lower than 20 cm. At 70 cm and greater, values are typically less than 0.05 mg OC m^{-2}.

Table 4.2: Calculated OC Loadings of the Silt and Clay Size Fractions (<63 µm) from the Münden 2 Profile

Depth (cm)	Horizon	Fraction (µm)	OC loading (mg m^{-2})
0-5	Ah	<63	NA
		<20	NA
		<6.3	NA
		<2	2.05
		<1	1.90
5-10	Al	<63	0.73
		<20	0.95
		<6.3	0.56
		<2	0.48
		<1	0.35
10-20	Al	<63	0.27
		<20	0.23
		<6.3	0.26
		<2	0.21
		<1	0.14
20-50	Sw-Al	<63	NA
		<20	0.08
		<6.3	0.09
		<2	0.13
		<1	0.11
50-70	Sd-Bt	<63	0.07
		<20	0.12
		<6.3	NA
		<2	NA
		<1	NA
70-90	sBtv	<63	0.02
		<20	0.03
		<6.3	0.06
		<2	0.03
		<1	0.02
90-110	sBv	<63	0.04
		<20	0.03
		<6.3	0.04
		<2	0.03
		<1	0.02

Table 4.2 (continued): Calculated OC Loadings of the Silt and Clay Size Fractions (<63 µm) from the Münden 2 Profile

110-140	IIiIsCv	<63	0.09
		<20	0.04
		<6.3	0.10
		<2	0.05
		<1	0.05
140-160+	IIiICv	<63	0.03
		<20	0.03
		<6.3	0.03
		<2	0.02
		<1	0.02

Again, the results suggest that sorptive processes onto mineral surfaces are not overly significant in the sequestration of organic material in this profile. This, of course, assumes that the ME level is an indicator of the importance of such processes.

4.5.3 Profile 3: Königstein

Similarly, OC loadings for the silt and clay size fractions are quite high for samples taken from the top 5 cm of the Königstein profile, due to the significant organic inputs at this site (see Table 4.3). OC loadings then continuously decline with depth. At a depth of 25 cm and more, values are <0.30 mg OC m^{-2} for all fractions, much less than the predicted ME level. Between 65 and 85 cm OC loadings increase slightly, particularly for the finer particle size fractions, compared to values calculated for depths of 45-65 cm. Calculated OC loadings for the Königstein profile do not support the hypothesis of a ubiquitous ME level for mineral surfaces.

4.5.4 Profile 4: Geinsheim

OC loadings calculated for silt and clay size fractions isolated from the Geinsheim profile, as shown in Table 4.4, are very low for all depths. In most cases, values are less than 0.10 mg OC m^{-2}, much lower than that required to cover the surface of the individual mineral particles. OC loadings already fall below 0.10 mg OC m^{-2} for the top 0-10 cm of the profile, which reflects the lack of inputs of litter to this profile. Despite the low loadings, amounts do, however, remain relatively consistent for all size separates throughout the depth of this profile.

Table 4.3: Calculated OC Loadings of the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile

Depth (cm)	Horizon	Fraction (µm)	OC loading (mg m^{-2})
0-5	Aeh	<63	2.82
		<20	3.84
		<6.3	NA
		<2	NA
		<1	1.58
5-10	Ahe-Bv	<63	1.23
		<20	1.00
		<6.3	0.94
		<2	0.58
		<1	0.59
10-25	Bv	<63	0.97
		<20	0.36
		<6.3	0.57
		<2	0.42
		<1	0.40
25-45	IIBv	<63	0.19
		<20	0.24
		<6.3	0.17
		<2	0.14
		<1	0.14
45-65	IIBv	<63	0.09
		<20	0.09
		<6.3	0.09
		<2	0.11
		<1	0.11
65-85	IIIBvCv	<63	0.10
		<20	0.09
		<6.3	0.16
		<2	0.23
		<1	0.23
85-100+	IViCv	<63	0.09
		<20	0.10
		<6.3	0.09
		<2	0.08
		<1	0.08

Table 4.4: Calculated OC Loadings of the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile

Depth (cm)	**Horizon**	**Fraction (µm)**	**OC loading (mg m^{-2})**
0-5	Ap	<63	0.07
		<20	0.08
		<6.3	0.08
		<2	0.07
		<1	0.08
5-10	Ap	<63	0.06
		<20	0.06
		<6.3	0.06
		<2	0.07
		<1	0.06
10-25	Ap	<63	0.06
		<20	0.12
		<6.3	0.06
		<2	0.07
		<1	0.06
25-50	M	<63	0.05
		<20	0.05
		<6.3	0.05
		<2	0.06
		<1	0.05
50-70	M	<63	0.06
		<20	0.06
		<6.3	0.06
		<2	0.08
		<1	0.07
70-90	IIP	<63	0.03
		<20	0.06
		<6.3	0.07
		<2	0.04
		<1	0.03
90-110	IIIfAxh-Go1	<63	0.07
		<20	0.06
		<6.3	0.03
		<2	0.03
		<1	0.04
110-130	IIIfAxh-Go2	<63	0.06
		<20	0.06
		<6.3	0.05
		<2	0.04
		<1	0.03
130-150+	IIIGro4	<63	0.06
		<20	0.08
		<6.3	0.07
		<2	0.05
		<1	0.05

4.5.5 Profile 5: Frankfurter Stadtwald

As shown in Table 4.5, the OC loadings for the silt and clay size fractions from the top 5 cm of the Frankfurter Stadtwald profile fall approximately within the ME range (i.e. 0.5 to 0.95 mg OC m^{-2}). These values are lower than expected given the high OC contents of the individual particle size fractions for this profile. This is due to the high surface area of the mineral component of these samples. OC loadings then decline very rapidly with depth, reaching values lower than that observed for most of the other profiles. At a depth of 25 cm and lower, OC loadings fall to 0.05 mg OC m^{-2} and below. At 85+ cm, OC loadings then begin to increase for all size separates (i.e. >0.10 mg OC m^{-2}), due to greater amounts of organic material present at these depths.

Table 4.5: Calculated OC Loadings of the Silt and Clay Size Fractions (<63 μm) from the Frankfurter Stadtwald Profile

Depth(cm)	Horizon	Fraction (μm)	OC loading (mg m^{-2})
0-5	Ah	<63	0.95
		<20	0.89
		<6.3	0.51
		<2	0.53
5-10	Ah	<63	0.89
		<20	1.09
		<6.3	NA
		<2	NA
10-15	AhGo	<63	0.30
		<20	0.30
		<6.3	0.26
		<2	0.26
15-20	AhGo	<63	0.21
		<20	0.20
		<6.3	0.18
		<2	0.15
20-25	AhGo	<63	0.06
		<20	0.06
		<6.3	0.06
		<2	0.06
25-30	Go1	<63	0.05
		<20	0.05
		<6.3	0.05
		<2	0.04
30-40	Go2	<63	0.04
		<20	0.03
		<6.3	0.03
		<2	0.03

Table 4.5 (continued): Calculated OC Loadings of the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile

Depth (cm)	**Horizon**	**Fraction (µm)**	**OC loading (mg m^{-2})**
40-50	Gro1	<63	0.03
		<20	0.03
		<6.3	0.02
		<2	0.02
50-60	Gro2	<63	0.01
		<20	0.01
		<6.3	0.01
		<2	0.01
60-70	Gro2	<63	NA
		<20	0.01
		<6.3	0.01
		<2	0.01
70-80	Gro3	<63	0.02
		<20	0.02
		<6.3	0.02
		<2	0.02
80-85	Gro3	<63	0.02
		<20	0.02
		<6.3	0.02
		<2	0.02
85-90	IIGr	<63	0.12
		<20	0.12
		<6.3	0.11
		<2	0.09
90-100	IIGr	<63	0.14
		<20	0.14
		<6.3	0.11
		<2	0.09
100-110	IIGr	<63	0.32
		<20	0.33
		<6.3	0.26
		<2	0.19

4.6 Dithionite- and Oxalate-Extractable Fe, Al and Mn

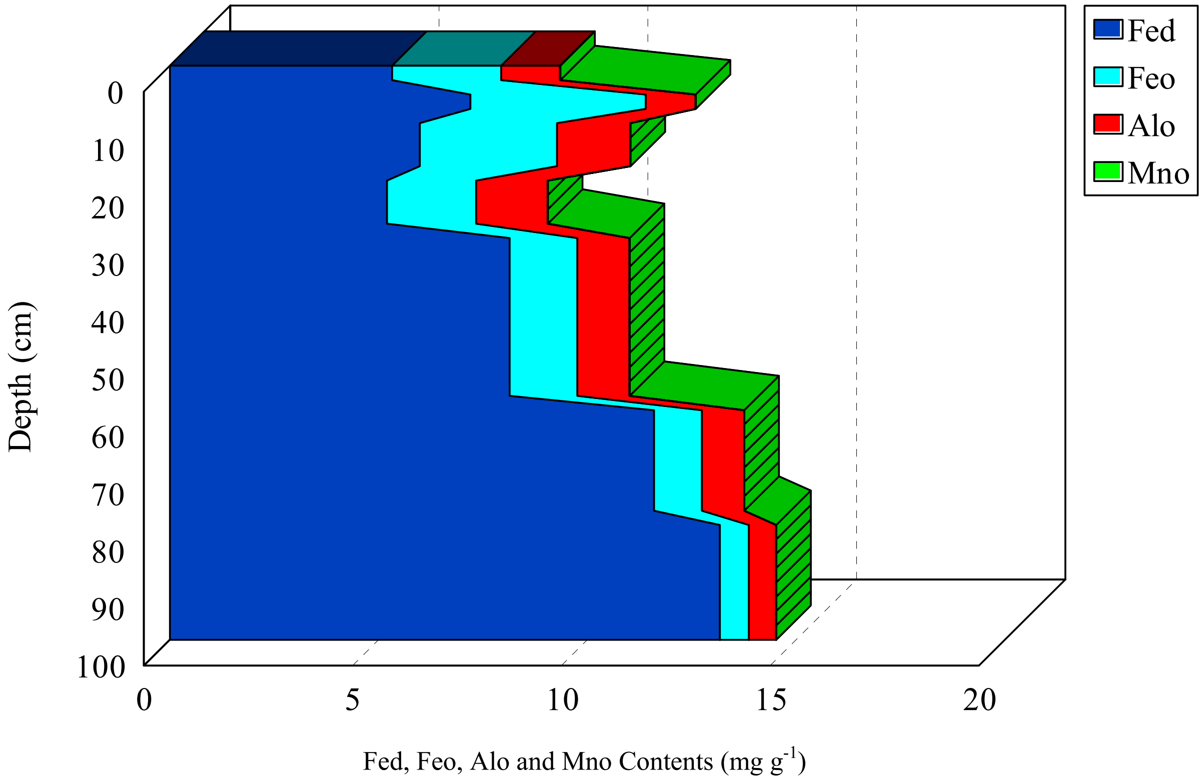
Analytical results for dithionite-extractable Fe (Fed) and oxalate -extractable Fe (Feo), Al (Alo) and Mn (Mno) in oxides present in the bulk soil samples (<2 mm) for the profiles investigated are detailed in Tables H.1 to H.5, Appendix H. Fed is an indicator of the amount of both crystalline and amorphous Fe oxides in samples, while oxalate only extracts Fe from non-crystalline forms. The results are also displayed graphically in Figures 4.33 to 4.37 below.

4.6.1 Profile 1: Münden 1

Fed increases significantly with profile depth, ranging from 5.33 mg g^{-1} for the top 5 cm sampled to 13.18 mg g^{-1} for the lowest depths of 80-100+ cm (see Figure 4.46). Measured Feo occurs in the greatest quantities at a depth of 5-10 cm (i.e. 4.20 mg g^{-1}). There is also a noticeable increase in Fed levels at this depth compared to that measured both above and below, likely related to podzolization processes and the related transport of Fe and Al with organic acids. Feo then progressively decreases with depth, reaching a profile low of 0.69 mg g^{-1} at 80-100+ cm. Considering the difference between Fed and Feo, it would appear that crystalline and amorphous forms of Fe occur in approximately equal quantities for the upper 5 cm of this profile. Amorphous forms are then found in slightly greater amounts at depths 5-20 cm. Below this, crystalline forms of Fe clearly dominate, occurring in increasingly greater amounts relative to amorphous Fe. Particularly at the lowest profile depths, samples contain significantly larger quantities of crystalline compared to amorphous Fe.

Alo, which occurs in lesser amounts compared to Feo, ranges from a high of 1.75 mg g^{-1} for samples of 10-20 cm to a low of 0.65 mg g^{-1} for the lowest depths of 80-100+ cm. Mn oxides are present in small quantities throughout the Münden 1 profile, as suggested by results for oxalate-extractable Mn. Measured Mno concentrations fall below 0.01 mg g^{-1} in all instances.

Figure 4.33: Dithionite- and Oxalate-Extractable Fe, Al and Mn (mg g^{-1}) in Bulk Samples (<2 mm) from the Münden 1 Profile as a Function of Depth

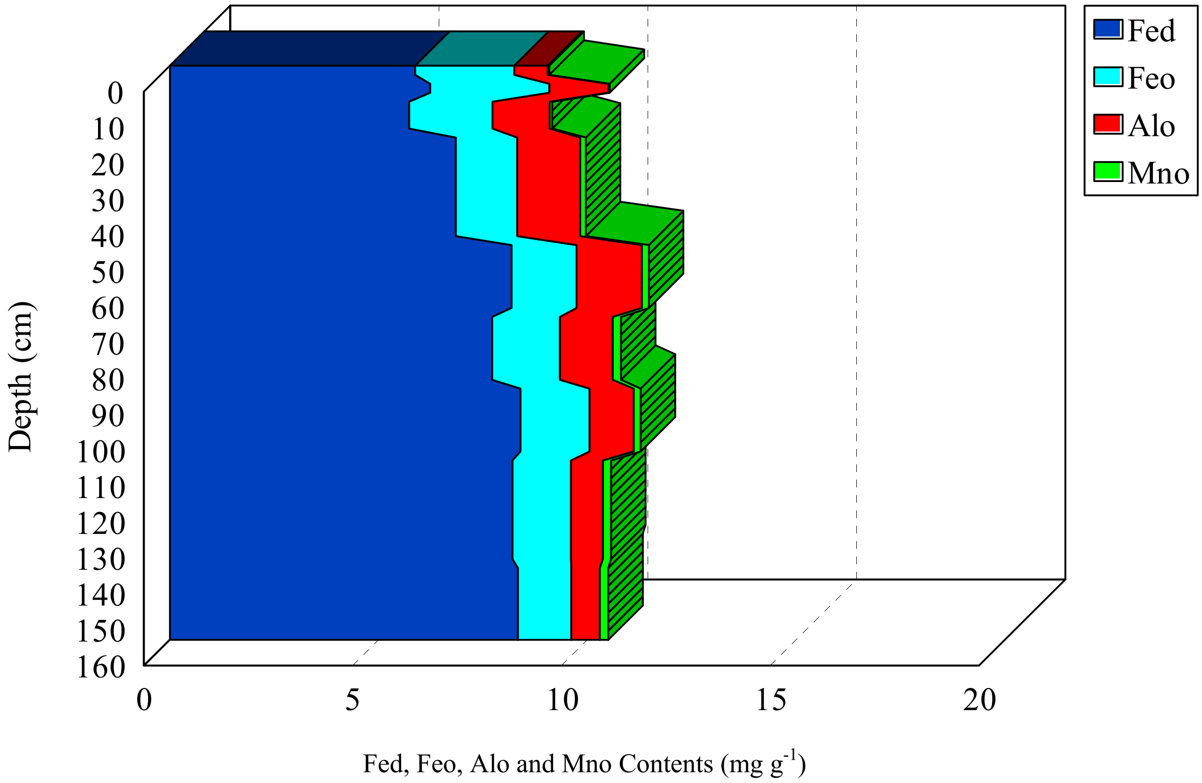


4.6.2 Profile 2: Münden 2

The Fed content of bulk samples analyzed from Münden 2 does not vary to the same extent as that for Münden 1 (see Figure 4.34). Fed slightly increases with depth, varying from 5.88 mg g^{-1} for 0-5 cm to 8.34 mg g^{-1} for the lowest depths of 140-160+ cm. In contrast, measured Feo decreases with increasing depth, varying from a high of 2.85 mg g^{-1} for 5-10 cm to a low of 1.28 mg g^{-1} for depths of 140-160+ cm. The results suggest that most of the Fe oxides present in this profile are crystalline in form, occurring in increasingly greater amounts with depth as the amorphous Fe content decreases.

Alo increases from 0.80 mg g^{-1} from the top of the profile to a high of 1.56 mg g^{-1} at depths of 50-70 cm. Interestingly, this depth (i.e. 50-70 cm) corresponds with elevated OC concentrations in bulk as well as in the fine particle size fractions (see Tables C.3 and C.5, Appendix C). Mno, which is present in the least quantities, increases somewhat with depth, ranging from a low of 0.073 mg g^{-1} (i.e. 0-5 cm) to 0.20 mg g^{-1} (140-160+ cm).

Figure 4.34: Dithionite- and Oxalate-Extractable Fe, Al and Mn (mg g^{-1}) in Bulk Samples (<2 mm) from the Münden 2 Profile as a Function of Depth

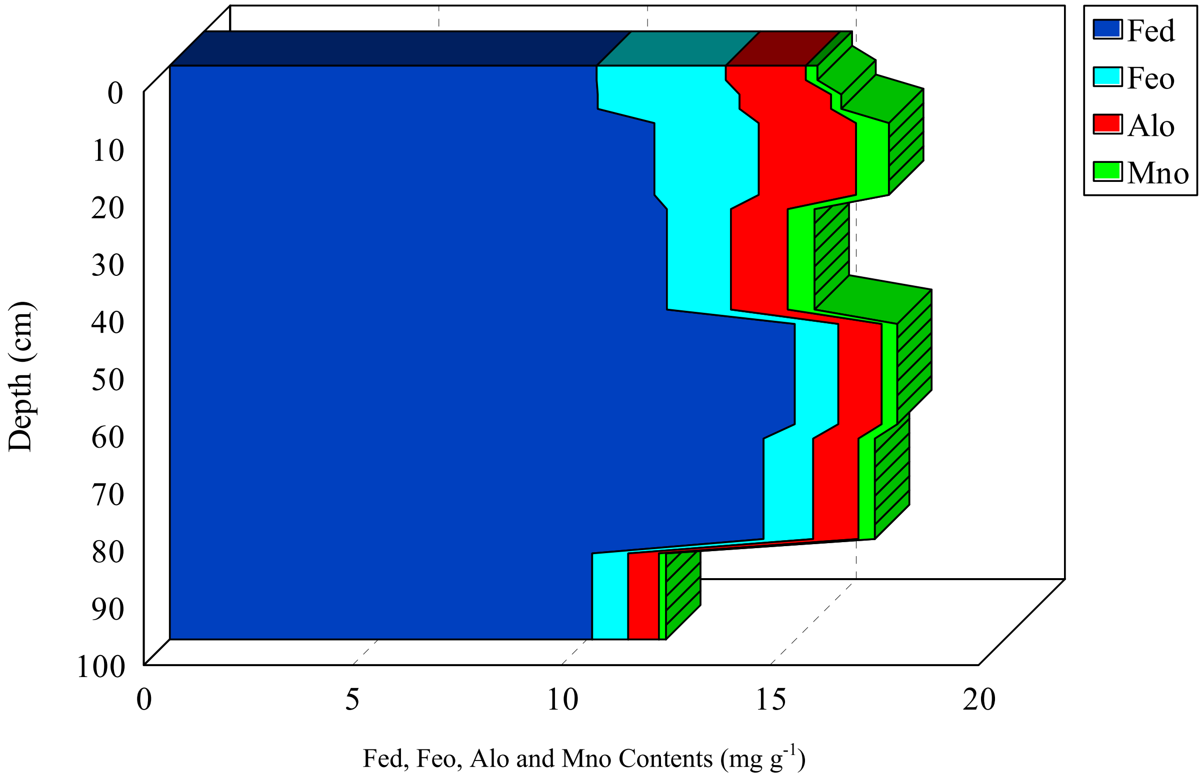


4.6.3 Profile 3: Königstein

Of all the profiles investigated, Königstein appears to contain the greatest amount of Fe oxides (see Figure 4.35). Measured Fed is greater than 10 mg g^{-1} for all profile depths, varying from 10.23 (i.e. 0-5 cm) to 14.98 (i.e. 45-65). At lower depths, Fed declines again to about 10 mg g^{-1} (IViCv horizon). A different trend can be observed for measured Feo. The greatest amounts are found at depths of 0-10 cm, with 3.09 and 3.39 mg Feo g^{-1}, respectively. Feo contents then generally decrease with profile depth, reaching a low of 0.86 mg Feo g^{-1} at 85-100+ cm. Clearly, the majority of the Fe oxides present in this profile are crystalline in form. Given the reflexes that were present at 21.3° 2Ø in the diffraction patterns for Königstein (see Figures F.5 and F.6, Appendix F), we can assume that goethite, a common Fe oxide found in soils, contributes significantly to the Fed values measured for this profile.

The greatest Alo contents were also measured for depths of 5-25 cm, with 2.19 and 2.33 mg g^{-1}, quantities higher than that observed for Münden 1 and 2. Alo then declines at lower depths, reaching a profile low of 0.74 mg g^{-1} at 85-100+ cm.

Figure 4.35: Dithionite- and Oxalate-Extractable Fe, Al and Mn (mg g^{-1}) in Bulk Samples (<2 mm) from the Königstein Profile as a Function of Depth

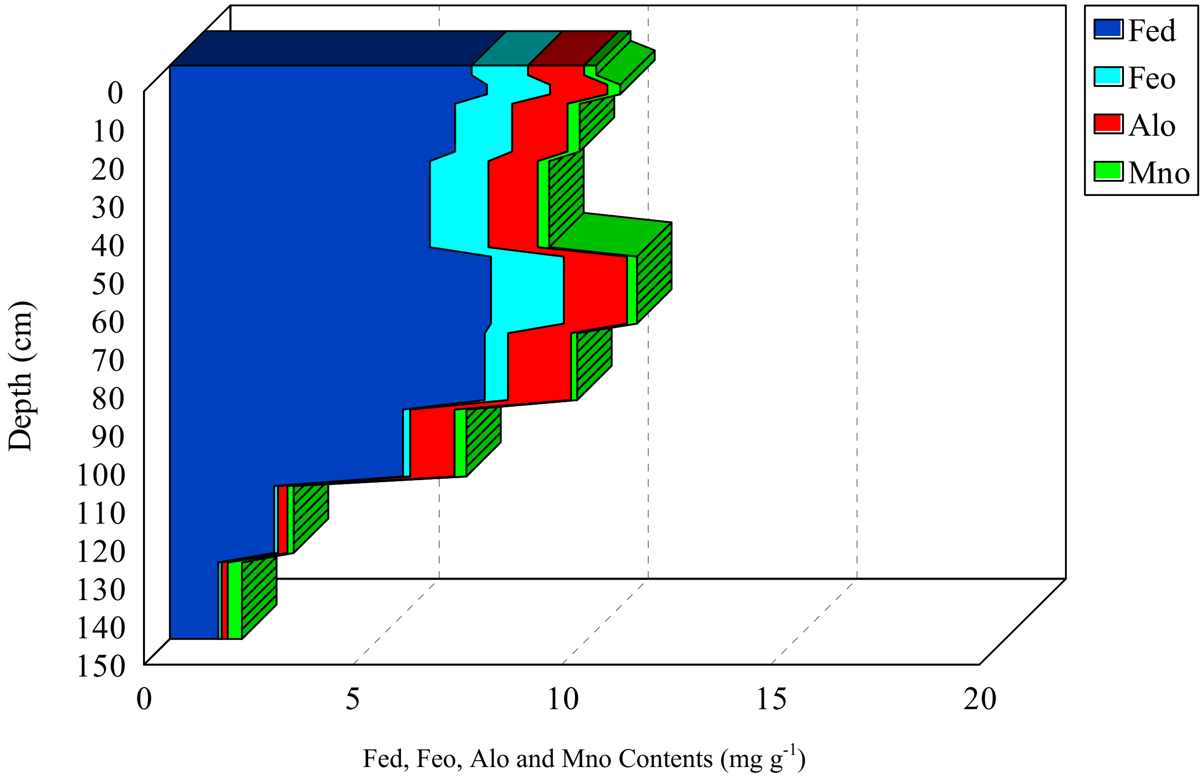


Similar to other profiles, Mn oxides are clearly not as important in quantitative terms relative to Fe and Al oxides. Mno contents ranged from a profile high of 0.79 mg g^{-1} for 10 to 25 cm to a low of 0.17 mg g^{-1} for the lowest sampled depths (i.e. 85 to 100+ cm).

4.6.4 Profile 4: Geinsheim

Figure 4.36 displays the contents of dithionite- and oxalate-extractable Fe, Al and Mn for Geinsheim. As shown, Fed levels fluctuate between 6.23 and 7.69 mg g^{-1} for bulk samples from depths of 0-90 cm. Below a depth of 110 cm, where groundwater influences are strong, Fed levels decline, reaching a profile low of 1.16 mg g^{-1} at the lowest depths of 130-150+ cm. Feo levels are below 2 mg g^{-1} for bulk samples between depths of 0-70 cm. At depths below 70 cm, Feo contents range from 0.56 to 0.08 mg g^{-1}. Similar to the other profiles, most of the Fe oxides present in the Geinsheim profile are crystalline.

Figure 4.36: Dithionite- and Oxalate-Extractable Fe, Al and Mn (mg g^{-1}) in Bulk Samples (<2 mm) from the Geinsheim Profile as a Function of Depth

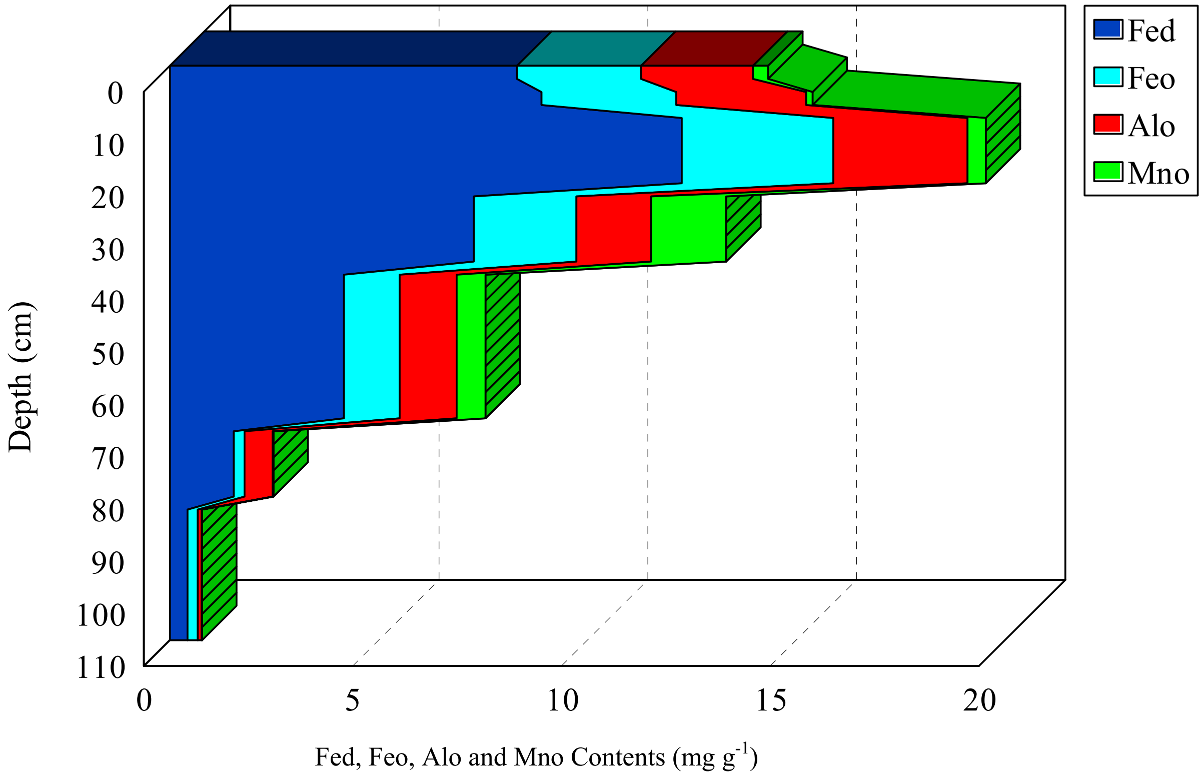


Alo contents vary from 1.3 to 1.4 mg g^{-1} in the top 25 cm of the profile. Levels then increase slightly at a depth of 50-90 cm, with amounts of >1.5 mg g^{-1}. Alo quantities then decrease to less than 0.5 mg g^{-1} for the lowest sampled depths (i.e. 130-150+ cm). Mno levels range from 0.14 (i.e. 70-90 cm) to 0.31 mg g^{-1} (i.e. 5-10 cm).

4.6.5 Profile 5: Frankfurter Stadtwald

Fed increases down to a depth of about 25 cm, with 8.32 and 12.26 mg g^{-1} for 0-5 and 10-25 cm, respectively (see Figure 4.37). Values for Fed then begin to decrease, reaching a profile low of 0.42 mg g^{-1} for the lowest sampled depths of 85-110 cm. Feo also increases slightly, from 2.97 to 3.63 mg g^{-1}, in samples from 0-25 cm. Below this depth, amounts then decline to 0.25 mg g^{-1} for the bottom of the profile. Relative to the other profiles, Frankfurter Stadtwald has the greatest quantities of Alo, as least at depths down to 25 cm (i.e. between 2.68 and 3.22 mg g^{-1}). Alo contents decrease at lower depths, reaching a profile low of 0.09 mg g^{-1} between 85 and 110 cm. In terms of Mn oxides, Mno peaks at 25-40 cm, with 1.79 mg g^{-1}. This is the highest observed concentration for all profiles investigated. Levels then decline significantly, reaching a profile low of less than 0.01 mg g^{-1} at depths greater than 70 cm.

Figure 4.37: Dithionite- and Oxalate-Extractable Fe, Al and Mn (mg g^{-1}) in Bulk Samples (<2 mm) from the Frankfurter Stadtwald Profile as a Function of Depth



5. Statistical Results

The following sections present the results of statistical analyses undertaken to identify possible relationships between the variables measured for the five soil profiles, as discussed in the previous chapter. An attempt was made to analyze topsoils (i.e. A horizon) apart from subsoils (i.e. B and C horizons) to avoid the potential for large organic matter inputs to the soil surface to bias results. In some cases, the limited number of samples, however, necessitated the analysis of whole soil profiles.

5.1 Soil Texture, Particle Size Separates and OC and N Contents and C:N Ratios

The relationship between organic matter, soil texture and certain particle size fractions based both particle size diameter and density has been a popular topic of study in the past (e.g. Turchenek and Oades 1979; Anderson et al. 1981; Tiessen and Stewart 1983; Balesdent et al. 1988; Cambardella and Elliot 1993; Buyanovsky et al. 1994). Such studies, of which temperate arable soils have often been the focus, indicate the existence of a relationship between particle size separate and organic matter content. Specifically, it has been found that the smaller particle size fractions, notably the fine silts and clays, typically contain the greatest amounts of organic matter relative to the other size separates. Further, many studies have also found that there is a positive correlation between clay and OC content in soils (e.g. Schimel 1985); that is, soils with a higher clay content have often been found to contain greater amounts of organic matter. In addition, clay content also appears to influence the turnover rate of organic carbon in soils (e.g. Ladd et al. 1985).

These apparent relationships between clay content and particle size separate and organic matter concentrations were tested for the soil profiles under investigation. The individual sampling sites were analyzed separately in terms of these parameters to avoid the possibility that relationships particular to certain profiles may be obscured when all are considered together. Topsoil samples could not be considered in isolation from the subsoil, as the number of samples was too small to provide a basis for an appropriate statistical analysis of parameters. Analyses were conducted though for the subsoils, to determine the extent to which results may deviate from those where both top- and subsoils were considered together. Given the number of subsoil samples in some instances though, caution must be exercised in the interpretation of results. It should be noted that statistical results are often presented for a low number of samples in soil sciences, where the work intensive nature of analyses inevitably forces the investigator to limit the sample size. Observed variations in the results between whole profiles and subsoils are discussed when found to be significantly different. Scatter plots of the variables OC, N and C:N and the percent clay and silt content of bulk samples which display statistically significant relationships are presented in Appendix I. Relationships in terms of the sand size fractions are not displayed in the form of scatter plots due to the insignificance of these fractions in terms of this study. The parameter labelled 'particle size fraction', which refers to the relationship between particle size and the OC and N content of each fraction, is also not presented in graphical form as it was defined as a nominal variable in the statistical analyses.

5.1.1 Profile: Münden 1

As shown in Table 5.1, only one independent variable, particle size fraction, correlates significantly with the OC and N contents of bulk samples from the Münden 1 profile.
The observed inverse relationship between this variable and OC and N content suggests that organic matter amounts generally increase with smaller particle size fractions. The correlations are, however, rather weak, with r values of only -0.267 ($p < 0.10$, $r^2 = 0.071$) and -0.446 ($p < 0.01$, $r^2 = 0.199$) between particle size fraction and OC and N content, respectively. The statistical results for these parameters do not vary to a large extent if the topsoil is excluded from analysis (i.e. 0-20 cm) (see Table 5.2). The relationship between particle size fraction and OC becomes only slightly stronger (i.e. -0.391 ($p<0.10$), $r^2 = 0.153$), while the correlation between particle size fraction and N content becomes less significant for the subsoil (i.e. $r = -0.411$ ($p < 0.10$), $r^2 = 0.169$). Overall, the OC and N content of bulk soil does not appear to be related or affected by clay content.

Table 5.1: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction	N= 42	N= 42	N= 40
- Correlation	**-0.267***	**-0.446*****	-0.140
- Significance	**0.087**	**0.003**	0.389
Sand (%)	N= 7	N= 7	N= 5
- Correlation	-0.383	-0.456	-0.224
- Significance	0.397	0.304	0.717
Silt (%)	N= 7	N= 7	N= 5
- Correlation	0.336	0.410	0.079
- Significance	0.461	0.361	0.900
Clay (%)	N= 7	N= 7	N= 5
- Correlation	-0.183	-0.258	-0.232
- Significance	0.694	0.576	0.707

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.2: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction	N=20	N=20	N=19
- Correlation	**-0.391***	**-0.411***	-0.228
- Significance	**0.088**	**0.072**	0.333
Sand (%)	N=4	N=4	N=3
- Correlation	-0.833	-0.913	0.192
- Significance	0.167	0.268	0.877
Silt (%)	N=4	N=4	N=3
- Correlation	0.836	0.918	0.204
- Significance	0.164	0.260	0.869
Clay (%)	N=4	N=4	N=3
- Correlation	-0.823	-0.912	-0.191
- Significance	0.177	0.269	0.878

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

According to the raw results for the individual size fractions (see Table C.3, Appendix C), the smallest size fractions, the fine silts and clays, consistently contain the greatest amounts of both OC and N compared to the other fractions. The weak correlations between OC and N contents and particle size fraction, and the lack of any observable relationship between these dependent variables and percent silt and clay, are likely a product of the particle size distribution of Münden 1 bulk samples. Specifically, these fractions make up only a relatively small proportion of bulk samples (i.e. about 6 to 10% and 15 to 26% for fine silts and clays, respectively) (see Table B.5, Appendix B). As a consequence, their overall contribution to the OC and N contents of bulk samples are relatively small.

5.1.2 Profile 2: Münden 2

Statistical analyses of the Münden 2 profile, as displayed in Table 5.3, also reveal an inverse relationship between particle size fraction and the OC and N contents of samples (i.e. $r= -0.259$ ($p< 0.10$), $r^2= 0.067$ and $r= -0.356$ ($p< 0.01$), $r^2= 0.127$, respectively). Similar to Münden 1, the correlations are rather weak and are likely due to the particle size distribution of bulk samples, as the raw results suggest that greater OC and N contents are associated with the smaller size fractions (see Table C.6, Appendix C). Especially clay proportions of bulk samples are not large enough to contribute to major differences in the OC and N concentrations of whole soils, hence yielding weak or nonexistent statistical relationships between these parameters. As shown in Table 5.4, the correlations between particle size fraction and OC and N contents become stronger and more statistically significant if the A horizon or top 0-5 cm is excluded from analysis (i.e. $r= -0.408$ ($p< 0.01$), $r^2= 0.166$ for OC and $r= -0.559$ ($p< 0.01$), $r^2= 0.312$ for N). This suggests that these relationships are stronger for greater depths in this profile.

Table 5.3: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N= 54 **-0.259*** **0.059**	N= 54 **-0.356***** **0.008**	N= 54 0.135 0.330
Sand (%) **- Correlation** **- Significance**	N= 9 0.332 0.398	N= 9 0.286 0.455	N= 9 0.310 0.417
Silt (%) **- Correlation** **- Significance**	N= 9 0.210 0.587	N= 9 0.188 0.629	N= 9 0.282 0.462
Clay (%) **- Correlation** **- Significance**	N= 9 -0.272 0.478	N= 9 -0.231 0.549	N= 9 -0.411 0.271

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.4: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N=40 **-0.408***** **0.009**	N=40 **-0.559***** **0.000**	N=40 -0.006 0.970
Sand (%) **- Correlation** **- Significance**	N=8 -0.105 0.805	N=8 **-0.686*** **0.060**	N=8 0.182 0.667
Silt (%) **- Correlation** **- Significance**	N=8 0.251 0.549	N=8 0.048 0.909	N=8 0.224 0.593
Clay (%) **- Correlation** **- Significance**	N=8 -0.262 0.531	N=8 0.202 0.631	N=8 -0.345 0.403

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.1.3 Profile 3: Königstein

Unlike the Münden profiles, Königstein does not exhibit a statistically significant relationship between particle size fraction and the OC content of samples (see Table 5.5), that is, there appears to be no progressive increase in OC contents with smaller size fractions. There is, however, a strong positive correlation between OC and the percent clay content of bulk samples (i.e. r= 0.843 ($p< 0.05$), r^2= 0.710). There is also a strong, highly significant correlation between the N and percent clay content of samples (i.e. r= 0.812 ($p< 0.05$), r^2= 0.659). As displayed in Table C.9, Appendix C, the clay fractions have noticeably more OC and N relative to the other particle size fractions. This correlation between the OC and N and percent clay content of bulk samples is, thus, likely a manifestation of the consistently high OC and N concentrations found in the smallest particle size fractions. Caution must be exercised, however, in the interpretation of this result. The correlations between OC and N and percent clay content could, in part, be an artefact of the fact that both OC and percent clay content of bulk samples decrease with depth. In addition, there is a strong positive correlation between the ratio of C:N and percent clay (i.e. r= 0.954 ($p< 0.01$), r^2= 0.910).

There is also a positive relationship between the percent silt content and C:N ratio of bulk samples from this profile (i.e. r= 0.798 ($p< 0.10$), r^2= 0.637). If topsoils are excluded from the analysis (i.e. 0-10 cm), however, the correlations between N content and percent clay and the ratio of C:N and percent silt lose their statistical significance (see Table 5.6). These relationships are, thus, not important for subsoil samples. The correlation between percent clay and OC concentrations and the ratio of C:N become even stronger when only the subsoil is considered (i.e. r= 0.936 ($p < 0.05$), r^2= 0.876 for OC and r= 0.903 ($p < 0.05$), r^2= 0.815).

In contrast to OC content, there is a statistically significant negative relationship between particle size fraction and N. The correlation coefficient is, however, only -0.357 ($p < 0.05$, r^2= 0.127), suggestive of a weak relationship. Both OC and N, as well as the ratio between the two, exhibit an inverse relationship with percent sand (i.e. r= -0.743 ($p < 0.10$), r^2= 0.552 for OC, r= -0.693 ($p < 0.10$), r^2= 0.480 for N and r= -0.932 ($p < 0.01$), r^2= 0.869 for C:N). The relationships between percent sand and OC and N are no longer significant when the A horizon is excluded from analysis (i.e. $p > 0.10$). This is likely a product of the methodology used to prepare soils for analysis. As only organic matter intimately associated with minerals or mineral complexes were of interest, the non- or partially-degraded light or macroorganic matter, which is usually associated with the sand size fraction, was removed manually prior to fractionation. The sand size fractions were, thus, depleted in organic matter.

Table 5.5: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction	N= 42	N= 42	N= 42
- Correlation	-0.147	**-0.357****	0.160
- Significance	0.354	**0.020**	0.310
Sand (%)	N= 7	N= 7	N= 7
- Correlation	**-0.743***	**-0.693***	**-0.932****
- Significance	**0.056**	**0.084**	**0.002**
Silt (%)	N= 7	N= 7	N= 7
- Correlation	0.527	0.463	**0.798***
- Significance	0.224	0.295	**0.031**
Clay (%)	N= 7	N= 7	N= 7
- Correlation	**0.843****	**0.812****	**0.954*****
- Significance	**0.017**	**0.026**	**0.001**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.6: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N=25 -0.294 0.154	N=25 **-0.566***** **0.003**	N=25 0.152 0.467
Sand (%) **- Correlation** **- Significance**	N=5 -0.787 0.114	N=5 -0.539 0.348	N=5 **-0.886**** **0.045**
Silt (%) **- Correlation** **- Significance**	N=5 0.607 0.278	N=5 0.340 0.575	N=5 0.788 0.113
Clay (%) **- Correlation** **- Significance**	N=5 **0.936**** **0.019**	N=5 0.750 0.144	N=5 **0.903**** **0.036**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.1.4 Profile 4: Geinsheim

Like the Münden profiles, there is a relatively weak, yet significant negative correlation between particle size fraction and the OC and N contents of samples from Geinsheim (i.e. r= -0.488 ($p< 0.01$), r^2= 0.238 for OC and r= -0.374 ($p< 0.01$), r^2= 0.140 for N) (see Table 5.7). This suggests that organic matter concentrations generally increase with progressively smaller particle size fractions. Again, there is a strong negative correlation between the percent sand and the OC and N contents of samples analyzed (i.e. r= -0.797 ($p< 0.01$), r^2= 0.635 for OC and r= -0.712 ($p< 0.05$), r^2= 0.507 for N). This is due to the minimal organic inputs at this site and corresponding lack of macroorganic matter, as opposed to being a product of the fractionation procedure used (i.e. removal of large pieces of particulate organic matter). Clearly, the site had not been cultivated for a while.

Silt content displays a significant positive relationship with both the OC and N concentration of bulk samples, with r values of 0.731 ($p< 0.05$, r^2= 0.534) for OC and 0.680 ($p< 0.05$, r^2= 0.462) for N. These relationships are even stronger in the case of percent clay, with r values of 0.807 ($p< 0.01$, r^2= 0.651) and 0.705 ($p< 0.05$, r^2= 0.497) for OC and N, respectively. This would indicate that the finer particle size fractions are enriched in organic matter. In contrast to Königstein, where there is the confounding factor that clay content decreases with depth along with OC, clay content of bulk samples for the Geinsheim profile remains rather stable to a depth of about 90 cm (i.e. between 44 and 52% (see Table B.20, Appendix B). It is, thus, safe to conclude that organic matter is likely protected when associated with the fine particle size separates of this soil profile. This, in turn, has an observable influence on the OC content of bulk samples. This is exemplified by OC values for depths of 25-50 cm and 50-70 cm, where concentrations increase from 12.97 g kg^{-1} to 15.49 g kg^{-1} (see Table C.10, Appendix C). Clay content also increases from 44 to 52% for these same depths, respectively.

Table 5.7: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N= 54 **-0.488***** **0.000**	N= 54 **-0.374***** **0.005**	N= 54 0.065 0.641
Sand (%) **- Correlation** **- Significance**	N= 9 **-0.797**** **0.010**	N= 9 **-0.712**** **0.031**	N= 9 -0.132 0.735
Silt (%) **- Correlation** **- Significance**	N= 9 **0.731**** **0.025**	N= 9 **0.680**** **0.044**	N= 9 0.075 0.847
Clay (%) **- Correlation** **- Significance**	N= 9 **0.807***** **0.009**	N= 9 **0.705**** **0.034**	N= 9 0.163 0.675

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

If the A horizon samples are excluded from analysis (i.e. 0-25 cm), the relationship between OC and particle size fraction remains approximately the same (see Table 5.8). The correlation between particle size fraction and N becomes, however, statistically insignificant (i.e. $p > 0.10$). Hence, it would appear that N content does not increase with progressively smaller particle size fractions in the subsoil of this profile. Additionally, the correlations observed for percent silt and OC and N contents are no longer significant at these depths. The relationships between OC and N and the percent clay contents of bulk samples essentially remain the same, however, with the exception that both correlations become less significant (i.e. $r= 0.816$ ($p< 0.05$), $r^2= 0.666$) for OC and $r= 0.741$ ($p< 0.10$; $r^2= 0.549$) for N). In light of these results, it would appear as if the percent clay content of bulk samples is a better predictor of organic matter concentrations than percent silt for the Geinsheim profile.

Table 5.8: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction	N=30	N=30	N=30
- Correlation	**-0.454****	-0.114	0.077
- Significance	**0.012**	0.550	0.687
Sand (%)	N=6	N=6	N=6
- Correlation	**-0.780***	-0.713	-0.363
- Significance	**0.067**	0.111	0.479
Silt (%)	N=6	N=6	N=6
- Correlation	0.650	0.587	0.316
- Significance	0.162	0.220	0.542
Clay (%)	N=6	N=6	N=6
- Correlation	**0.816****	**0.741***	0.384
- Significance	**0.048**	**0.092**	0.452

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.1.5 Profile 5: Frankfurter Stadtwald

Similar to the other profiles, there is a negative correlation between the variables particle size fraction and N content for samples from Frankfurter Stadtwald (see Table 5.9). An r value of -0.217 ($p< 0.10$, $r^2= 0.047$) is small, however, indicative of a weak relationship. The positive correlation between particle size fraction and the ratio of C:N is stronger and highly significant (i.e. $r= 0.518$ ($p< 0.01$), $r^2= 0.268$) and suggests that the smaller size particle fractions are enriched in more degraded forms of organic matter relative to the other size separates. The percent sand content of bulk samples is also positively related to the ratio of C:N, albeit rather weakly, with an r of 0.496 ($p< 0.10$, $r^2= 0.246$). The percent clay content of bulk samples exhibits a negative correlation with the ratio of C:N (i.e. $r= -0.528$ ($p< 0.10$), $r^2= 0.279$). This relationship, together with that between particle size fraction and C:N, indicates an N enrichment of the clay fraction. As shown in Table 5.10, all of the above observed relationships lose their statistical significance, however, when the A horizon or topsoil is not considered in analyses (i.e. 0-25 cm). It would, thus, appear that none of the independent variables have an effect on the OC and N contents of bulk subsoil samples for this profile.

Table 5.9: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Samples (<2 mm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N= 76 -0.001 0.995	N= 76 **-0.217*** **0.060**	N= 76 **0.518***** **0.000**
Sand (%) **- Correlation** **- Significance**	N= 15 -0.299 0.278	N= 15 -0.295 0.286	N= 14 **0.496*** **0.071**
Silt (%) **- Correlation** **- Significance**	N= 15 0.297 0.283	N= 15 0.289 0.296	N= 14 -0.451 0.105
Clay (%) **- Correlation** **- Significance**	N= 15 0.297 0.283	N= 15 0.295 0.285	N= 14 **-0.528*** **0.052**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.10: Correlation Coefficients for the Variables Particle Size Fraction and Distribution and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Particle Size Fraction **- Correlation** **- Significance**	N=40 -0.014 0.931	N=40 -0.179 0.268	N=40 0.246 0.125
Sand (%) **- Correlation** **- Significance**	N=10 -0.406 0.244	N=10 -0.220 0.542	N=9 0.446 0.229
Silt (%) **- Correlation** **- Significance**	N=10 0.331 0.351	N=10 0.147 0.684	N=9 -0.398 0.288
Clay (%) **- Correlation** **- Significance**	N=10 0.468 0.172	N=10 0.282 0.429	N=9 -0.481 0.190

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.2 Clay Mineral Composition and the OC and N Contents and C:N Ratios of Clay Samples

As suggested by the results of various studies presented in the literature, the clay mineral suite of a soil appears to be an influential factor in its ability to stabilize organic matter. Certain clay minerals are more likely to react with or have the capacity to bind organic substances than others. In particular, the swelling 2:1 layer clays, notably smectites, are often identified as being more reactive and capable of binding substantial amounts of organic matter (see Greenland 1965a, b; Mortland 1970; Theng 1974). This capacity is particularly attributed to this mineral's large surface area, most of which is found in the internal layer. The results of statistical analyses conducted on the clay composition estimated for the clay particle size fraction from each profile and the OC, N and C:N measured for bulk samples are presented below. Although estimates of the clay composition of samples are difficult to quantify, and should, thus, be interpreted with caution, such an analysis helps to provide an indication of the relative importance of different clay minerals for each site. Results for the OC and N contents of the respective clay fractions were used for the analysis, as opposed to that for bulk samples, given the potential for relationships among whole soils to be biased by variability in clay content. All profiles were first analyzed together, both with and without topsoils, to obtain an impression of the relative significance of certain clay minerals, notably smectites, in terms of the OC concentrations between soils. Analyses were then conducted for each site separately, both for whole profiles and subsoils. Scatter plots of the clay minerals which positively correlate with the OC and N contents and ratios of C:N for the whole profile of each respective site in a statistically significant manner are displayed in Appendix J, while the results are presented below.

5.2.1 A Comparison of All Profiles

As displayed in Table 5.11, only kaolinite exhibits a positive relationship with the OC content of clay when the top- and subsoil samples of all profiles are considered (i.e. $r= 0.266$ ($p< 0.10$), $r^2= 0.071$). Although this is a very weak correlation, it is surprising as kaolinite is normally expected to have a low capacity to protect organic matter, given its low SSA (i.e. 15 to 30 $m^2\ g^{-1}$ (AG Boden 1994)) and low surface reactivity due to its neutral charge. This clay mineral has been shown, however, to have broken edges with exposed hydroxyl groups which are highly reactive (Theng 1974; Tan 1988). These edges, which can make up as much as 20% of the SSA of this mineral, are able to bind organic material and contribute to the sequestration capacity of a soil. Kaolinite also positively correlates with the ratio of C:N, with an r value of 0.514 (p< 0.01) and an r^2 of 0.264. This suggests that kaolinite is associated with less degraded forms of organic matter. Interestingly, smectite, which has been demonstrated to adsorb substantial amounts of organic compounds, correlates negatively with the OC content of clay samples (i.e. r= -0.265 (p< 0.10), r^2= 0.070). As will be shown later, this result can be attributed to the inclusion of the Frankfurter Stadtwald profile in the analysis. Specifically, an increase in the OC contents of the finer particle size fractions at the lowest depths of this profile (see Table C.14, Appendix C), where groundwater influences are significant, and a corresponding decrease in the smectite content of samples (see Table E.10, Appendix E) yields this negative relationship.

Table 5.11: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (<2 μm) of all Profiles (Top- and Subsoils)

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite	N= 47	N= 47	N= 47
- Correlation	**-0.265***	-0.169	-0.129
- Significance	**0.072**	0.257	0.388
Vermiculite	N= 47	N= 47	N= 47
- Correlation	0.059	-0.116	**0.332****
- Significance	0.693	0.438	**0.023**
Mixed Layer	N= 47	N= 47	N= 47
- Correlation	-0.003	0.214	**-0.317****
- Significance	0.985	0.149	**0.030**
Illite	N= 47	N= 47	N= 47
- Correlation	-0.087	0.107	**-0.343****
- Significance	0.561	0.473	**0.018**
Chlorite	N= 47	N= 47	N= 47
- Correlation	-0.130	-0.136	-0.065
- Significance	0.384	0.362	0.663
Kaolinite	N= 47	N= 47	N= 47
- Correlation	**0.266***	-0.079	**0.514*****
- Significance	**0.071**	0.599	**0.000**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

In addition, vermiculite exhibits a weak positive correlation with the ratio of C:N (i.e. r= 0.332 (p< 0.05), r^2= 0.110), due to the presence of this mineral in the upper layers of the Münden and Königstein profiles (see Tables E.6, E.7 and E.8, Appendix E). In contrast, mixed layer and illite minerals are negatively correlated with C:N (i.e. r= -0.317 (p< 0.05), r^2= 0.100 and -0.343 (p< 0.05), r^2= 0.118), albeit also rather weakly.

When the topsoil samples are excluded from analysis, different relationships emerge (see Table 5.12). Vermiculite is the only mineral which positively correlates with the OC content of clay subsoil samples (i.e. r= 0.365 ($p< 0.05$), r^2= 0.133). This relationship is, however, weak. The negative correlation between illite and the ratio of C:N (i.e. r= -0.339 ($p< 0.10$) r^2= 0.115) remains, likely a result of the tendency of this mineral to be present in the largest quantities at the bottom of the soil profiles, where organic material is highly degraded. Smectite minerals do not appear to stabilize organic matter in subsoils, as reflected by the absence of a statistically significant correlation between this mineral and OC concentrations.

Table 5.12: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (<2 µm) of all Profiles

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite **- Correlation** **- Significance**	N= 33 -0.089 0.620	N= 33 -0.147 0.415	N= 33 0.128 0.477
Vermiculite **- Correlation** **- Significance**	N= 33 **0.365**** **0.037**	N= 33 0.256 0.150	N= 33 0.253 0.156
Mixed Layer **- Correlation** **- Significance**	N= 33 -0.059 0.746	N= 33 0.079 0.664	N= 33 -0.252 0.158
Illite **- Correlation** **- Significance**	N= 33 -0.241 0.176	N= 33 -0.119 0.511	N= 33 **-0.339*** **0.053**
Chlorite **- Correlation** **- Significance**	N= 33 -0.049 0.786	N= 33 0.015 0.934	N= 33 -0.054 0.767
Kaolinite **- Correlation** **- Significance**	N= 33 0.104 0.566	N= 33 -0.052 0.772	N= 33 0.259 0.145

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.2.2 Profile: Münden 1

As displayed in Table 5.13, only mixed layer minerals, most likely an illite/smectite complex, correlate significantly with OC and N contents when the whole profile is considered (i.e. 0.801 ($p< 0.05$), r^2= 0.642) and 0.879 ($p< 0.01$), r^2= 0.773). The amount of mixed layer minerals decrease with depth, as do organic matter concentrations (see Tables E.6, Appendix E and C.3, Appendix C). There could be an association between organic matter and this clay mineral species. The correlations appear, however, to be a result of the data set. As shown in the scatter plots J.2 and J.3, Appendix J, the inclusion of one data point (an A horizon sample) has clearly led to these significant relationships. Upon exclusion of the A horizon, the observed correlations become insignificant (i.e. $p> 0.10$) (see Table 5.14). Vermiculite exhibits a highly significant positive correlation with the ratio of C:N, with an r value of 0.795 ($p< 0.05$) and an r^2 of 0.632, indicating an association with less degraded forms of organic material in this profile. Illite and kaolinite are negatively correlated with the ratio of C:N, with -0.959 ($p< 0.01$, $r^2= 0.920$) and -0.783 ($p< 0.05$, $r^2= 0.613$) for the former and latter minerals, respectively. The quantities of both minerals generally increase with depth (see Table E.11, Appendix E). The ratio of C:N also declines with depth, hence the negative correlation.

Table 5.13: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (<2 µm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite **- Correlation** **- Significance**	N= 7 0.276 0.549	N= 7 0.124 0.791	N= 6 **0.795**** **0.033**
Mixed Layer **- Correlation** **- Significance**	N= 7 **0.801**** **0.030**	N= 7 **0.879**** **0.009**	N= 6 0.425 0.342
Illite **- Correlation** **- Significance**	N= 7 **-0.743*** **0.056**	N= 7 -0.665 0.103	N= 6 **-0.959**** **0.001**
Chlorite **- Correlation** **- Significance**	N= 7 -0.508 0.245	N= 7 -0.502 0.251	N= 6 -0.215 0.643
Kaolinite **- Correlation** **- Significance**	N= 7 -0.538 0.213	N= 7 -0.463 0.295	N= 6 **-0.783**** **0.037**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

A strong positive correlation between vermiculite and OC emerges (i.e. r= 0.916 ($p<0.10$), r^2= 0.839) when only the subsoil is analysed, while that between this mineral and the ratio of C:N becomes stronger (i.e. r= 0.991 ($p<0.01$), r^2= 0.992). The negative relationship between illite and OC is even stronger and more significant at lower depths (i.e. r= -0.958 ($p< 0.05$), r^2= 0.918). Illite and N and C:N also significantly correlate in a negative manner (i.e. r= -0.939 ($p<0.10$), r^2= 0.882 and r= -0.954 ($p<0.05$), r^2= 0.910, respectively). Given the sample size for the Münden 1 subsoil, however, particularly with respect to the ratio of C:N, these results are not reliable.

Table 5.14: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (<2 µm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite **- Correlation** **- Significance**	N= 4 **0.916*** **0.084**	N= 4 0.859 0.141	N= 3 **0.991***** **0.009**
Mixed Layer **- Correlation** **- Significance**	N= 4 0.573 0.427	N= 4 0.565 0.435	N= 3 0.602 0.398
Illite **- Correlation** **- Significance**	N= 4 **-0.958**** **0.042**	N= 4 **-0.939*** **0.061**	N= 3 **-0.954**** **0.046**
Chlorite **- Correlation** **- Significance**	N= 4 0.342 0.658	N= 4 0.318 0.682	N= 3 0.431 0.569
Kaolinite **- Correlation** **- Significance**	N= 4 -0.463 0.537	N= 4 -0.389 0.611	N= 3 -0.640 0.360

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.2.3 Profile 2: Münden 2

According to the results of analyses for samples from the entire Münden 2 profile, as displayed in Table 5.15, none of the clay minerals identified for this profile are positively associated with the OC and N contents of clay size separates. The only statistically significant relationship that exists is a negative one between chlorite and N, with an r of -0.589 ($p< 0.10$, $r^2= 0.347$). As with Münden 1, chlorite increases somewhat with depth down to about 70 cm, where amounts fluctuate between 5 and 7% (see Table E.7, Appendix E). N is clearly depth dependent, decreasing with depth, resulting in a relatively strong correlation. A causal relationship cannot be assumed.

When the A horizon is excluded from analysis, a strong positive relationship is observed between vermiculite and N (i.e. r= 0.725 ($p<0.05$), $r^2= 0.526$) (see Table 5.16). Illite is clearly not associated with organic material at lower depths in this profile, as reflected by the strong significant negative correlations between this mineral and OC (i.e. r= -0.822 ($p< 0.05$), $r^2= 0.676$), N (i.e. r= -0.891 ($p< 0.01$), $r^2= 0.794$) and C:N (i.e. r= -0.668 ($p<0.10$), $r^2= 0.446$). Given the results, we can assume that clay minerals at this site have a low capacity to stabilise organic matter.

Table 5.15: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (<2 µm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite	N= 9	N= 9	N= 9
- Correlation	-0.243	-0.266	0.158
- Significance	0.528	0.488	0.685
Mixed Layer	N= 9	N= 9	N= 9
- Correlation	0.025	-0.001	-0.058
- Significance	0.950	0.997	0.882
Illite	N= 9	N= 9	N= 9
- Correlation	-0.169	-0.121	-0.570
- Significance	0.663	0.756	0.109
Chlorite	N= 9	N= 9	N= 9
- Correlation	-0.518	**-0.589***	0.146
- Significance	0.153	**0.095**	0.707
Kaolinite	N= 9	N= 9	N= 9
- Correlation	0.350	0.344	0.001
- Significance	0.356	0.365	0.999

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.16: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (<2 µm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite	N= 8	N= 8	N= 8
- Correlation	0.600	**0.725****	0.404
- Significance	0.115	**0.042**	0.321
Mixed Layer	N= 8	N= 8	N= 8
- Correlation	0.025	-0.075	0.055
- Significance	0.953	0.860	0.896
Illite	N= 8	N= 8	N= 8
- Correlation	**-0.822****	**-0.891*****	**-0.668***
- Significance	**0.012**	**0.003**	**0.071**
Chlorite	N= 8	N= 8	N= 8
- Correlation	0.510	0.363	0.613
- Significance	0.197	0.377	0.106
Kaolinite	N= 8	N= 8	N= 8
- Correlation	-0.167	-0.289	-0.200
- Significance	0.693	0.487	0.634

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.2.4 Profile 3: Königstein

Similar to the Münden 2 profile, OC does not positively correlate with any of the clay minerals in samples from Königstein when all horizons are considered together (see Table 5.17). There is a highly significant negative correlation between chlorite and OC (i.e. r= -0.895 ($p < 0.01$), r^2= 0.801) and N (i.e. r= -0.951 ($p < 0.01$), r^2= 0.904) contents. This correlation may be a reflection of the clay mineral dynamics and is not necessarily an indicator of the protective capacity of clay minerals (i.e. pedogenic chlorite occurs in increasingly greater quantities with profile depth, while OC displays the opposite pattern). N contents positively correlate with vermiculite (i.e. r= 0.741 ($p < 0.10$), r^2= 0.549). Vermiculite appears in the greatest quantities in the top 25 cm of the profile (see Table E.8, Appendix E) and could be a product of the weathering of chlorite, which has been reported to turn into both vermiculite and smectite (Olson et al. 2000).

Table 5.17: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (< 2 µm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite	N= 7	N= 7	N= 7
- Correlation	0.569	**0.741***	0.205
- Significance	0.182	**0.057**	0.659
Mixed Layer	N= 7	N= 7	N= 7
- Correlation	0.395	0.537	0.114
- Significance	0.381	0.214	0.807
Illite	N= 7	N= 7	N= 7
- Correlation	-0.437	-0.581	-0.310
- Significance	0.327	0.172	0.499
Chlorite	N= 7	N= 7	N= 7
- Correlation	**-0.895*****	**-0.951*****	-0.565
- Significance	**0.007**	**0.001**	0.187
Kaolinite	N= 7	N= 7	N= 7
- Correlation	0.609	0.628	0.571
- Significance	0.147	0.131	0.180

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

For the B and C horizons of the Königstein profile, the relationship between vermiculite and N is stronger and more significant (i.e. r= 0.896 ($p < 0.05$), r^2= 0.803) (see Table 5.18). A strong positive correlation between this mineral and OC also emerges (i.e. r= 0.855 ($p < 0.10$), r^2= 0.731). Kaolinite correlates even more strongly with OC (i.e. r= 0.992 ($p < 0.01$), r^2= 0.984) and N (i.e. r= 0.824 ($p < 0.10$), r^2= 0.679). Interestingly, an increase in the OC concentrations of the clay size fractions between 65 and 85 cm in this profile corresponds to elevated levels of kaolinite at this same depth (see Table C.9, Appendix C and Table E.8, Appendix E). This suggests that kaolinite may help protect organic material at this site. Illite and chlorite are clearly not associated with organic material in the subsoil, as reflected by strong negative correlations with OC (i.e. r= -0.917 ($p< 0.05$), r^2= 0.841 for illite and r= -0.987 ($p<0.01$), r^2= 0.974 for chlorite) and N (i.e. r= -0.896 ($p< 0.05$), r^2= 0.803 for illite and r= -0.869 ($p< 0.01$), r^2= 0.755 for chlorite).

Table 5.18: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (< 2 µm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Vermiculite	N= 5	N= 5	N= 5
- Correlation	**0.855***	**0.896****	-0.086
- Significance	**0.065**	**0.040**	0.890
Mixed Layer	N= 5	N= 5	N= 5
- Correlation	0.445	0.610	-0.056
- Significance	0.453	0.275	0.929
Illite	N= 5	N= 5	N= 5
- Correlation	**-0.917****	**-0.896****	-0.284
- Significance	**0.029**	**0.040**	0.644
Chlorite	N= 5	N= 5	N= 5
- Correlation	**-0.987*****	**-0.869****	-0.297
- Significance	**0.002**	**0.056**	0.625
Kaolinite	N= 5	N= 5	N= 5
- Correlation	**0.992*****	**0.824***	0.463
- Significance	**0.001**	**0.086**	0.432

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.2.5 Profile 4: Geinsheim

Although there is a significant proportion of smectite minerals in the Geinsheim profile, there does not appear to be any relationship between its presence and the OC and N contents of clay samples (see Table 5.19). Mixed layer illite/smectite correlates positively, however, with OC (i.e. r= 0.644 ($p< 0.10$), r^2= 0.415), as well as N (i.e. r= 0.623 ($p< 0.10$), r^2= 0.388). There is also a highly significant positive correlation between kaolinite and the OC (i.e. r= 0.920 ($p< 0.01$), r^2= 0.846) and N (r= 0.745 ($p< 0.05$), r^2= 0.555) contents of clay samples. As previously mentioned, this clay mineral is normally not expected to have much of a capacity to protect organic matter. Illite exhibits a positive relationship with N (i.e. 0.667 ($p< 0.50$), r^2= 0.445), but is negatively correlated with the ratio of C:N (i.e. r= -0.620 ($p< 0.10$), r^2= 0.384).

Table 5.19: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (<2 µm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite	N= 9	N= 9	N= 9
- Correlation	0.052	-0.153	0.321
- Significance	0.895	0.694	0.399
Mixed Layer	N= 9	N= 9	N= 9
- Correlation	**0.644***	**0.623***	-0.384
- Significance	**0.061**	**0.073**	0.308
Illite	N= 9	N= 9	N= 9
- Correlation	0.537	**0.667****	**-0.620***
- Significance	0.136	**0.049**	**0.075**
Chlorite	N= 9	N= 9	N= 9
- Correlation	**-0.703****	-0.360	-0.119
- Significance	**0.035**	0.341	0.761
Kaolinite	N= 9	N= 9	N= 9
- Correlation	**0.920*****	**0.745****	-0.362
- Significance	**0.000**	**0.021**	0.338

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.20: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (<2 µm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite	N= 6	N= 6	N= 6
- Correlation	0.400	0.217	0.225
- Significance	0.432	0.680	0.668
Mixed Layer	N= 6	N= 6	N= 6
- Correlation	**0.818****	0.561	0.122
- Significance	**0.047**	0.247	0.819
Illite	N= 6	N= 6	N= 6
- Correlation	0.157	0.543	-0.626
- Significance	0.767	0.266	0.184
Chlorite	N= 6	N= 6	N= 6
- Correlation	-0.694	-0.295	-0.469
- Significance	0.126	0.570	0.348
Kaolinite	N= 6	N= 6	N= 6
- Correlation	**0.909****	**0.824***	-0.082
- Significance	**0.012**	**0.044**	0.878

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

When only the subsoil is considered (see Table 5.20), the strength of the relationship between kaolinite and OC remains approximately the same (i.e. $r= 0.909$ ($p< 0.05$), $r^2= 0.826$), while that with N becomes slightly stronger (i.e. $r= 0.824$ ($p< 0.05$), $r^2= 0.679$). The correlation between mixed layer minerals and OC is also stronger in the subsoil (i.e. $r= 0.818$ ($p< 0.05$),

r^2= 0.669). This mineral is no longer significantly related to N, however (i.e. $p > 0.10$). The same holds true for illite.

5.2.6 Profile 5 : Frankfurter Stadtwald

As displayed in Table 5.21, illite correlates significantly with both the OC and N content of clay samples from the entire Frankfurter Stadtwald profile (i.e. r= 0.515 ($p < 0.10$), r^2= 0.265 and r= 0.589 ($p < 0.05$), r^2= 0.347, respectively). Smectite on the other hand, exhibits a negative relationship with OC (i.e. r= -0.595 ($p < 0.50$), r^2= 0.354) and N (i.e. r= -0.590 ($p < 0.05$), r^2= 0.348). This suggests that low organic matter contents coincide with higher smectite contents and vice versa, in opposition to that which would be normally expected. Caution must be exercised, however, in the interpretation of the results for both illite and smectite. As already mentioned, strong groundwater influences in this profile, especially below a depth of 80-85 cm, may yield atypical results. The negative correlation between smectite content and OC and N holds, however, when the results are re-examined after the elimination of samples from greater than 80 cm, with an r of -0.599 ($p < 0.10$, r^2= 0.359) for OC and an r of -0.629 ($p < 0.10$, r^2= 0.396) for N (not shown).

Table 5.21: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Clay Size Fractions (<2 µm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite **- Correlation** **- Significance**	N= 15 **-0.595**** **0.019**	N= 15 **-0.590**** **0.021**	N= 15 -0.238 0.393
Mixed Layer (Illite/Smectite) **- Correlation** **- Significance**	N= 15 -0.088 0.756	N= 15 -0.088 0.754	N= 15 -0.168 0.548
Illite **- Correlation** **- Significance**	N= 15 **0.515*** **0.050**	N= 15 **0.589**** **0.021**	N= 15 0.183 0.515
Chlorite **- Correlation** **- Significance**	N= 15 0.438 0.103	N= 15 0.248 0.373	N= 15 **0.609**** **0.016**
Kaolinite **- Correlation** **- Significance**	N= 15 0.098 0.728	N= 15 -0.180 0.521	N= 15 **0.820***** **0.000**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

When the A horizon is excluded from analysis (see Table 5.22), very strong positive relationships develop between illite and OC (i.e. r= 0.919 (p< 0.01), r^2= 0.845), N (i.e. r= 0.851 (p< 0.01), r^2= 0.724) and C:N (i.e. r= 0.947 (p< 0.01), r^2= 0.897). Strong positive correlations are also observed between chlorite and OC (i.e. r= 0.925 (p< 0.01), r^2= 0.856), N (i.e. r= 0.932 (p<0.01), r^2= 0.869) and C:N (i.e. r= 0.800 (p< 0.01), r^2== 0.640). The same also holds true for kaolinite and all three independent variables (i.e. r= 0.839 (p< 0.01), r^2= 0.704 for OC, r= 0.827 (p< 0.01), r^2= 0.684 for N and r= 0.850 (p< 0.01), r^2= 0.723). Due to the groundwater influences at the bottom of this profile and the related increase in organic matter, we cannot assume, however, that these observed correlations are reflective of real relationships. Rather, the results are likely depth-related, with increased organic matter amounts occurring independently of larger concentrations of these minerals present at these depths.

Table 5.22: Correlation Coefficients for Clay Minerals and OC, N and C:N for the Subsoil Clay Size Fractions (<2 µm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Smectite **- Correlation** **- Significance**	N= 10 **-0.608*** **0.062**	N= 10 **-0.719**** **0.019**	N= 10 -0.519 0.125
Mixed Layer (Illite/Smectite) **- Correlation** **- Significance**	N= 10 **-0.575*** **0.082**	N= 10 -0.431 0.214	N= 10 **-0.655**** **0.040**
Illite **- Correlation** **- Significance**	N= 10 **0.919***** **0.000**	N= 10 **0.851***** **0.002**	N= 10 **0.947***** **0.000**
Chlorite **- Correlation** **- Significance**	N= 10 **0.925***** **0.000**	N= 10 **0.932***** **0.000**	N= 10 **0.800***** **0.005**
Kaolinite **- Correlation** **- Significance**	N= 10 **0.839***** **0.002**	N= 10 **0.827***** **0.003**	N= 10 **0.850***** **0.002**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

In comparing the results between profiles, the lack of a statistically significant positive correlation between most clay minerals and the OC and N contents of all profiles suggests that the clay minerals present generally have a minimal impact on the stabilisation of organic matter. Only vermiculite in the Münden 1 and Königstein subsoils, mixed layer minerals in the Geinsheim profile and especially kaolinite in the Königstein subsoil and Geinsheim profile would appear to be associated with organic matter. Not even smectite minerals, which are often emphasized as having a large capacity to protect or stabilize organic carbon, exhibit a positive relationship with OC and N for the Geinsheim and Frankfurter Stadtwald profiles. This, of course, does not unequivocally mean, however, that clay minerals do not play a role in protecting organic matter in the profiles of concern. They may, for instance, be involved in building complexes with oxides and exchangeable cations which serve to stabilize organic materials. Certain clay minerals may also have a greater capacity than others in protecting organic compounds, relationships which may not observable in such an analysis due to the inaccuracies involved in quantifying clay mineral amounts. Nonetheless, the observed relationships are much weaker than that often reported in the literature. Specific surface area is perhaps a better predictor of the relationship between clay minerals and organic matter and the importance of sorption processes. This will be addressed in Section 5.5.

5.3 Exchangeable Cations and OC and N Contents and C:N Ratios

Although Cation Exchange Capacity (CEC) is a typical parameter that is measured for soils, the relationship between cation concentrations or percent cation saturation and organic carbon contents is often neglected. As cations readily react with organic matter to form stable complexes (Mortvedt 2000), they are likely to play a significant role in binding organic substances to minerals, forming organic-cation-mineral complexes which help to sequester OC. The major cations suggested to serve as bridges between organic materials and minerals are Ca^{2+} and Mg^{2+} in alkaline soils and Al^{3+} and Fe^{3+} in acidic soils (Oades 1988). The presence of cations also promotes the flocculation of clay minerals which helps to protect organic matter. A statistical analysis of the relationship between the percent cation saturation and OC and N content of the soils under investigation was conducted to determine the extent to which certain cations may be bound to organic matter, perhaps serving as bridges in the complexation of organic substances with minerals. Scatter plots of the various cations that exhibit a statistically significant positive correlation with the OC and N contents of bulk soils for the whole soil profiles, and the ratios thereof, are shown in Appendix K. Topsoils could not be analysed separately from subsoils for the individual profiles due to the limited number of samples available. Subsoil samples were also analysed to confirm results for the whole profiles but must be interpreted with caution due to the low sample number. Information regarding the percent cation saturation of bulk samples from the Frankfurter Stadtwald profile was unfortunately not available to conduct such an analysis.

5.3.1 Profile 1: Münden 1

Statistical analyses of the results for the Münden 1 profile reveal several relationships between certain exchangeable cations and OC and N (see Table 5.23). Of the base cations, Ca displays the strongest, most significant positive relationship with OC (i.e. r= 0.915 (p< 0.01), r^2= 0.837), as well as with N (r= 0.915 (p< 0.01), r^2= 0.837). Mg also exhibits a positive relationship with the OC content of bulk samples (i.e. r= 0.673 (p< 0.10), r^2= 0.453), albeit less significant and strong as that between Ca and OC. Both Ca and Mg occur in the greatest amounts in the upper 5 cm of soil at this site and decrease progressively with depth, as do the OC and N contents (see Table D.3, Appendix D). These cations appear to be present in rather small amounts and are, thus, unlikely to play an important role in relative terms in this soil with respect to reacting with organic substances to form stable complexes. This is supported by the fact that these significant relationships disappear when the topsoil is excluded from analysis (i.e. p> 0.10) (see Table 5.24).

Table 5.23: Correlation Coefficients for % Cation Saturation and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na	N= 7	N= 7	N= 6
- Correlation	-0.141	-0.113	-0.372
- Significance	0.763	0.809	0.468
K	N= 7	N= 7	N= 6
- Correlation	-0.255	-0.310	-0.378
- Significance	0.581	0.499	0.460
Mg	N= 7	N= 7	N= 6
- Correlation	**0.673***	0.658	0.257
- Significance	**0.098**	0.108	0.623
Ca	N= 7	N= 7	N= 6
- Correlation	**0.915*****	**0.915*****	0.454
- Significance	**0.004**	**0.004**	0.366
Fe	N= 7	N= 7	N= 6
- Correlation	0.369	0.304	**0.812****
- Significance	0.416	0.507	**0.049**
Mn	N= 7	N= 7	N= 6
- Correlation	0.408	0.434	0.143
- Significance	0.364	0.330	0.788
Al	N= 7	N= 7	N= 6
- Correlation	**-0.909*****	**-0.889*****	-0.720
- Significance	**0.005**	**0.007**	0.107
H	N= 7	N= 7	N= 6
- Correlation	**0.733***	**0.740***	0.535
- Significance	**0.061**	**0.057**	0.274

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Al and H ions are present in the greatest quantities in this profile. Al correlates negatively, however, with both OC (i.e. $r = -0.909$ ($p < 0.01$), $r^2 = 0.826$) and N (i.e. $r = -0.889$ ($p < 0.01$), $r^2 = 0.790$) and is, thus, not associated with organic matter. H ions would appear to be positively related to organic material, as indicated by correlations of 0.733 ($p < 0.10$, $r^2 = 0.537$) and 0.740 ($p < 0.10$, $r^2 = 0.548$) with OC and N, respectively. Fe correlates significantly with the ratio of C:N (i.e. $r = 0.812$ ($p < 0.05$), $r^2 = 0.659$) and would, thus, appear to be associated with less degraded forms of organic material. As the highest C:N ratios occur in the top layers of the profile, where Fe saturation is at its greatest (see Table D.1, Appendix D), this relationship is not surprising. When only the subsoil for this profile is considered, Fe strongly correlates with OC concentrations (i.e. $r = 0.928$ ($p<0.10$), $r^2 = 0.861$) (see Table 5.24). Hence, Fe cations would appear to be associated with organic material at greater depths.

Table 5.24: Correlation Coefficients for the Variables % Cation Saturation and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na **- Correlation** **- Significance**	N= 4 -0.199 0.801	N= 4 -0.076 0.924	N= 3 0.017 0.989
K **- Correlation** **- Significance**	N= 4 -0.892 0.108	N= 4 **-0.994***** **0.006**	N= 3 -0.701 0.506
Mg **- Correlation** **- Significance**	N= 4 -0.895 0.105	N= 4 **-0.996***** **0.004**	N= 3 -0.681 0.523
Ca **- Correlation** **- Significance**	N= 4 -0.597 0.403	N= 4 -0.852 0.148	N= 3 -0.017 0.989
Fe **- Correlation** **- Significance**	N= 4 **0.928*** **0.072**	N= 4 0.684 0.316	N= 3 0.846 0.358
Mn **- Correlation** **- Significance**	N= 4 -0.236 0.764	N= 4 -0.462 0.538	N= 3 -0.017 0.989
Al **- Correlation** **- Significance**	N= 4 -0.775 0.225	N= 4 -0.429 0.571	N=3 -0.936 0.229
H **- Correlation** **- Significance**	N= 4 **0.912*** **0.088**	N= 4 0.651 0.349	N= 3 0.930 0.239

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.3.2: Profile 2: Münden 2

As shown in Table 5.25, most of the exchangeable cations do not appear to be significantly associated with organic matter in the Münden 2 profile. Only Fe displays a positive relationship with OC. With a correlation of 0.586 (r^2= 0.343) and a p value of <0.10, however, this relationship is neither strong nor highly significant. While K is negatively correlated with the ratio of C:N (i.e. r = -0.584 (p< 0.10), r^2= 0.341), H exhibits a positive relationship with this variable (i.e. r= 0.593 (p< 0.10), r^2= 0.352).

Table 5.25: Correlation Coefficients for % Cation Saturation and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na **- Correlation** **- Significance**	N= 9 -0.094 0.810	N= 9 -0.059 0.879	N= 9 -0.484 0.187
K **- Correlation** **- Significance**	N= 9 -0.071 0.855	N= 9 -0.018 0.964	N= 9 **-0.584*** **0.098**
Mg **- Correlation** **- Significance**	N= 9 -0.314 0.410	N= 9 -0.281 0.464	N= 9 -0.574 0.106
Ca **- Correlation** **- Significance**	N= 9 -0.246 0.523	N= 9 -0.216 0.576	N= 9 -0.538 0.135
Fe **- Correlation** **- Significance**	N= 9 **0.586*** **0.097**	N= 9 0.554 0.121	N= 9 0.568 0.111
Mn **- Correlation** **- Significance**	N= 9 0.242 0.530	N= 9 0.235 0.543	N= 9 0.067 0.864
Al **- Correlation** **- Significance**	N= 9 0.115 0.769	N= 9 0.086 0.825	N= 9 0.465 0.207
H **- Correlation** **- Significance**	N= 9 0.360 0.341	N= 9 0.327 0.390	N= 9 **0.593*** **0.092**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

When the topsoil is excluded from analysis, Al correlates significantly with both OC (i.e. r= 0.683 (p< 0.10), r2= 0.466) and N (i.e. r= 0.625 (p< 0.10), r2= 0.391) (see Table 5.26). H is also positively correlated with OC in the subsoil of this profile (i.e. r= 0.718 (p< 0.10), r2= 0.516). Both Al and H cations would, thus, appear to be associated with organic material at lower depths in the Münden 2 profile.

Table 5.26: Correlation Coefficients for the Variables % Cation Saturation and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na **- Correlation** **- Significance**	N= 8 **-0.694*** **0.056**	N= 8 -0.555 0.153	N= 8 -0.540 0.167
K **- Correlation** **- Significance**	N= 8 **-0.750**** **0.032**	N= 8 -0.376 0.359	N= 8 **-0.670*** **0.069**
Mg **- Correlation** **- Significance**	N= 8 **-0.700*** **0.053**	N= 8 -0.554 0.154	N= 8 -0.537 0.170
Ca **- Correlation** **- Significance**	N= 8 **-0.709**** **0.049**	N= 8 **-0.630*** **0.094**	N= 8 -0.526 0.180
Fe **- Correlation** **- Significance**	N= 8 0.378 0.356	N= 8 0.008 0.985	N= 8 0.414 0.307
Mn **- Correlation** **- Significance**	N= 8 -0.200 0.635	N= 8 -0.407 0.316	N= 8 -0.069 0.870
Al **- Correlation** **- Significance**	N= 8 **0.683*** **0.062**	N= 8 **0.625*** **0.097**	N= 8 0.507 0.200
H **- Correlation** **- Significance**	N= 8 **0.718**** **0.045**	N= 8 0.585 0.128	N= 8 0.541 0.166

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.3.3 Profile 3: Königstein

As shown in Table 5.27, many exchangeable cations are very strongly related with the OC and N contents of bulk samples in the Königstein profile. Both Mg and Ca display highly significant correlations with OC, with r values of 0.936 ($p< 0.01$, $r^2= 0.876$) and 0.977 ($p< 0.01$, $r^2= 0.955$), respectively. There is also a strong positive relationship between these cations and N (i.e. $r= 0.939$ ($p< 0.01$), $r^2= 0.882$ for Mg and $r= 0.976$ ($p< 0.01$), $r^2= 0.953$ for Ca). Similar to the Münden 1 profile, Mg and Ca occur in the largest quantities in the top layers of the profile, along with organic concentrations (see Table D.9, Appendix D). While Ca correlates positively with the ratio of C:N (i.e. $r= 0.717$ ($p< 0.10$), $r^2= 0.514$), Mg does not. Of the acid cations, Fe displays the strongest positive relationship with OC (i.e. $r= 0.943$ ($p< 0.01$) $r^2= 0.889$), as well as with N (i.e. 0.947 ($p< 0.01$), $r^2= 0.897$) and C:N (i.e. 0.717 ($p< 0.10$), $r^2= 0.514$). The relationship between Mn and OC, N and C:N is not quite as strong or significant, with r values of 0.750 ($p< 0.10$, $r^2= 0.563$), 0.708 ($p< 0.10$, $r^2= 0.501$) and 0.728

($p < 0.10$, $r^2 = 0.530$), respectively. Like Münden 1, Al is negatively correlated with OC (i.e. r= -0.871 ($p < 0.05$), $r^2 = 0.759$) and N (i.e. r= -0.887 ($p < 0.01$), $r^2 = 0.787$). H ions also display a significant negative relationship with OC (i.e. r= -0.779 ($p < 0.05$), $r^2 = 0.607$), N (i.e. r= -0.739 ($p < 0.10$), $r^2 = 0.546$), as well as with C:N (i.e. r= -0.858 ($p < 0.05$), $r^2 = 0.736$). These cations are, thus, not associated with organic material in this profile. When only the subsoil is considered though, most of the significant relationships observed between cations and OC, N and C:N disappear (i.e. $p < 0.10$) (see Table 5.28). For Ca and OC and N, however, the exclusion of the outliers from the A horizon does not alter the relationship to any great extent. Given the low sample number (i.e. N= 5) when topsoil samples are excluded from the analysis, however, these results must be interpreted with care.

Table 5.27: Correlation Coefficients for % Cation Saturation and OC, N and C:N of Bulk Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na **- Correlation** **- Significance**	N= 7 0.371 0.413	N= 7 0.343 0.451	N= 7 0.233 0.616
K **- Correlation** **- Significance**	N= 7 0.195 0.676	N= 7 0.261 0.571	N= 7 -0.336 0.462
Mg **- Correlation** **- Significance**	N= 7 **0.936***** **0.002**	N= 7 **0.939***** **0.002**	N= 7 0.656 0.110
Ca **- Correlation** **- Significance**	N= 7 **0.977***** **0.000**	N= 7 **0.976***** **0.000**	N= 7 **0.717*** **0.070**
Fe **- Correlation** **- Significance**	N= 7 **0.943***** **0.001**	N= 7 **0.947***** **0.001**	N= 7 **0.717*** **0.070**
Mn **- Correlation** **- Significance**	N= 7 **0.750*** **0.052**	N= 7 **0.708*** **0.075**	N= 7 **0.728*** **0.064**
Al **- Correlation** **- Significance**	N= 7 **-0.871**** **0.011**	N= 7 **-0.887***** **0.008**	N= 7 0.509 0.244
H **- Correlation** **- Significance**	N= 7 **-0.779**** **0.039**	N= 7 **-0.739*** **0.058**	N= 7 **-0.858**** **0.013**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.28: Correlation Coefficients for the Variables % Cation Saturation and OC, N and C:N of Bulk Subsoil Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na	N= 5	N= 5	N= 5
- Correlation	-0.234	-0.353	-0.038
- Significance	0.705	0.560	0.952
K	N= 5	N= 5	N= 5
- Correlation	**-0.832***	-0.554	**-0.936****
- Significance	**0.081**	0.333	**0.019**
Mg	N= 5	N= 5	N= 5
- Correlation	-0.078	-0.033	-0.027
- Significance	0.900	0.958	0.965
Ca	N= 5	N= 5	N= 5
- Correlation	**0.946****	**0.884****	0.768
- Significance	**0.015**	**0.047**	0.130
Fe	N= 5	N= 5	N= 5
- Correlation	0.297	0.371	0.068
- Significance	0.627	0.539	0.914
Mn	N= 5	N= 5	N= 5
- Correlation	0.455	0.220	0.671
- Significance	0.442	0.723	0.215
Al	N= 5	N= 5	N= 5
- Correlation	0.672	0.458	0.709
- Significance	0.214	0.438	0.180
H	N= 5	N= 5	N= 5
- Correlation	-0.746	-0.551	-0.763
- Significance	0.148	0.336	0.134

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.3.4 Profile 4: Geinsheim

With respect to the Geinsheim profile, only Na and K correlate positively with OC contents in bulk samples, with a value of 0.745 ($p< 0.05$, $r^2= 0.555$) for the former and 0.777 ($p< 0.05$, $r^2= 0.604$) for the latter (see Table 5.29). Both cations also correlate with N contents (i.e. $r= 0.715$ ($p< 0.05$), $r^2= 0.511$) and $r= 0.881$ ($p< 0.01$), $r^2= 0.776$). Na and K would, thus, appear to be associated with organic material in this profile. Such cations are, however, unlikely to lead to the long-term preservation of organic matter as they only form weak bonds (Scheffer and Schachtschabel 2002). The aggregates formed through such an association are, hence, unstable. K may promote flocculation of the clay minerals though, resulting in the physical protection of organic material. Na generally serves, however, to disperse particles, hence its usefulness as a dispersive agent in a variety of soil science methods, exposing organic material in aggregates to mineralization.

Table 5.29: Correlation Coefficients for % Cation Saturation and OC, N and C:N for Bulk Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na	N= 9	N= 9	N= 9
- Correlation	__0.745**__	__0.715**__	0.056
- Significance	**0.021**	**0.031**	0.885
K	N= 9	N= 9	N= 9
- Correlation	__0.777**__	__0.881***__	-0.265
- Significance	**0.014**	**0.002**	0.490
Mg	N= 9	N= 9	N= 9
- Correlation	__-0.733**__	__0.659*__	-0.071
- Significance	**0.025**	**0.054**	0.855
Ca	N= 9	N= 9	N= 9
- Correlation	0.228	-0.037	0.324
- Significance	0.556	0.924	0.395

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Only the positive relationships between Na and K and OC remain significant when the subsoil is analysed (i.e. r= 0.836 (p< 0.05), r^2= 0.699 for Na and OC and r= 0.754 (p< 0.10), r^2= 0.569 for K and OC) (see Table 5.30). These cations no longer significantly correlate with N, however (i.e. p> 0.10). Interestingly, Ca and Mg do not display any relationship with OC contents, the two cations which occur in the greatest amounts in this profile and which are most often suggested as playing the most important role in forming complexes with organic substances (e.g. Oades 1988). In fact, Mg displays a negative correlation with OC (i.e. r= -0.733 (p< 0.05), r^2= 0.537). This cation correlates positively though with N (i.e. r= 0.659 (p< 0.10), r^2= 0.434).

Table 5.30: Correlation Coefficients for the Variables % Cation Saturation and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Na **- Correlation** **- Significance**	N= 6 **0.836**** **0.038**	N= 6 0.591 0.217	N= 6 0.533 0.276
K **- Correlation** **- Significance**	N= 6 **0.754*** **0.083**	N= 6 0.414 0.415	N= 6 0.623 0.186
Mg **- Correlation** **- Significance**	N= 6 -0.494 0.320	N= 6 -0.143 0.787	N= 6 -0.464 0.354
Ca **- Correlation** **- Significance**	N= 6 0.376 0.463	N= 6 0.056 0.915	N= 6 0.388 0.448

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Overall, exchangeable cations do not appear to be as intimately associated with organic substances in the investigated soils as would be suggested in the literature. In the Münden 1 and 2 subsoils, Fe and Al cations appear to be associated with organic matter. Particularly in the case of Münden 1 though, the number of subsoil samples do not allow for reliable conclusions to be made. Ca appears to be the most important cation in the Königstein soil in terms of organic matter stabilisation. Neither Ca nor Mg appear to be associated with organic material in the Geinsheim profile, relationships which would be expected given the results in the literature. Only Na and K significantly correlate with organic substances in this profile. In the case of Na though, organic matter is unlikely to be protected. Of course, a correlation between certain exchangeable cations and organic substances does not mean that OC or N is automatically protected. Cations are believed to play a role in protecting organic matter by serving as a bridge for organic substances to negatively charged clay minerals, yielding stable complexes which reduce mineralization rates. Thus, in order to shed light on the question of whether exchangeable cations are important in the formation of organo-mineral complexes, the association between these exchangeable cations and the individual clay minerals present in the profiles must also be examined. This will be the focus of the next section.

5.4 Percent Cation Saturation and Clay Mineral Composition

Although cations readily react with organic matter in soils, this, in itself, does not necessarily lead to its automatic protection and sequestration. Cations may serve as bridges between minerals and organic compounds, however, which results in aggregation formation and consequent organic matter stabilisation. To fully understand how exchangeable cations may protect organic matter, it is, thus, important to examine how the mineral composition also correlates with cation concentrations or saturation, an indicator of potential cation bridging between minerals and organic compounds. The statistical analyses conducted on the relationship between percent cation saturation and the clay mineral composition determined for each of the profiles of concern are presented below. Analyses were only conducted on whole profiles. Scatter plots of the percent saturation of those cations which display a significant positive correlation with the variables OC, N and C:N are presented in Appendix L. All statistical results are displayed in the Tables 5.31 to 5.34 below.

5.4.1 Profile 1: Münden 1

Several significant relationships emerge between clay minerals and cations in the Münden 1 soil profile (see Table 5.31). Vermiculite correlates significantly with Fe, with an r value of 0.847 ($p< 0.05$, $r^2= 0.717$), while mixed layer illite/smectite exhibits a strong positive relationship with Ca (i.e. $r= 0.883$ ($p< 0.01$), $r^2= 0.780$). The former relationship would appear to be of greater importance, however, in terms of the protection of organic matter. Specifically, both vermiculite and Fe appear to be associated with OC in the subsoil of this profile. A significant relationship between Ca and OC only appears to exist when the whole soil profile is considered. The same holds true for mixed layer illite/smectite. Particularly in the latter case, the positive relationship appears to be the result of the data set (i.e. outliers). K is strongly correlated with the minerals illite (i.e. $r= 0.846$ ($p< 0.05$), $r^2= 0.716$) and kaolinite (i.e. $r= 0.855$ ($p< 0.05$), $r^2= 0.731$). Neither these two minerals nor K are, however, significantly related to OC and N in this profile and are, thus, unlikely to play a role in the stabilisation of organic materials.

Table 5.31: Correlation Coefficients for % Cation Saturation and Clay Minerals Identified for the Münden 1 Profile

	Clay Mineral				
Cation	**Vermiculite**	**Mixed Layer**	**Illite**	**Chlorite**	**Kaolinite**
Na	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.515	0.081	0.382	0.379	0.213
- Significance	0.237	0.863	0.397	0.401	0.646
K	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.743*	-0.306	**0.846****	-0.504	**0.855****
- Significance	0.056	0.504	**0.016**	0.249	**0.014**
Mg	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.618	0.659	0.129	-0.650	0.249
- Significance	0.139	0.107	0.783	0.114	0.590
Ca	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.289	**0.883*****	-0.303	-0.568	-0.137
- Significance	0.529	**0.008**	0.509	0.184	0.769
Fe	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	**0.847****	-0.023	-0.718*	-0.299	-0.546
- Significance	**0.016**	0.961	0.069	0.515	0.205
Mn	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.678*	0.544	0.238	-0.370	0.355
- Significance	0.094	0.207	0.608	0.414	0.434
Al	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.171	-0.735*	-0.657	0.562	0.281
- Significance	0.714	0.060	0.109	0.190	0.541
H	N= 7	N= 7	N= 7	N= 7	N= 7
- Correlation	0.210	0.664	-0.676*	-0.300	0.267
- Significance	0.652	0.104	0.095	0.513	0.563

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.4.2 Profile 2: Münden 2

As shown in Table 5.32, only illite and K exhibit a statistically significant positive relationship, with a correlation of 0.810 ($p < 0.01$) and an r^2 of 0.656. The association of K with illite is of course expected, as this cation is commonly present in the interlayer space of this clay mineral (Bailey 1980; Moore and Reynolds 1997). However, neither illite nor K is positively related to OC and N contents in this profile. Fe displays a relatively weak relationship with OC for the whole soil profile. Al positively correlates with OC and N in the subsoil of this profile. Neither of these two cations are associated with clay minerals in this profile, however. This suggests that Fe and Al is singularly associated with organic matter in this soil or that other minerals such as oxides build complexes with this exchangeable cation and carbon, leading to its stabilization.

Table 5.32: Correlation Coefficients for % Cation Saturation and Clay Minerals Identified for the Münden 2 Profile

	Clay Mineral				
Cation	**Vermiculite**	**Mixed Layer**	**Illite**	**Chlorite**	**Kaolinite**
Na	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.445	0.190	0.563	-0.388	0.448
- Significance	0.230	0.625	0.114	0.302	0.226
K	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.559	-0.032	**0.810*****	-0.421	0.177
- Significance	0.118	0.934	**0.008**	0.259	0.649
Mg	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.349	0.215	0.574	-0.229	0.282
- Significance	0.358	0.578	0.106	0.553	0.461
Ca	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.330	0.046	0.562	-0.346	0.394
- Significance	0.385	0.906	0.115	0.361	0.294
Fe	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	0.257	0.168	-0.663*	-0.102	0.181
- Significance	0.504	0.665	0.051	0.794	0.641
Mn	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.365	-0.170	0.508	-0.700**	0.522
- Significance	0.334	0.662	0.163	0.036	0.149
Al	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	0.326	-0.171	-0.475	0.454	-0.407
- Significance	0.392	0.661	0.196	0.219	0.277
H	N= 9	N= 9	N= 9	N= 9	N= 9
- Correlation	0.345	-0.060	-0.620*	0.188	-0.320
- Significance	0.363	0.879	0.075	0.629	0.401

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.4.3 Profile 3: Königstein

Several clay minerals identified for the Königstein profile exhibit significant positive relationships with the percent saturation of a number of cations (see Table 5.33). Similar to the Münden 1 soil, vermiculite, which occurs in greater quantities in the upper horizons of the Königstein profile, positively correlates with Fe (i.e. $r= 0.742$ ($p< 0.10$), $r^2= 0.551$). Mixed layer illite/smectite displays a positive correlation with Mn, with an r of 0.697 ($p< 0.10$) and an r^2 of 0.486. Illite correlates with both K (i.e. $r= 0.719$ ($p< 0.10$), $r^2= 0.517$) and H (i.e. $r= 0.758$ ($p< 0.05$), $r^2= 0.575$). Of the clay minerals, only vermiculite positively correlates with measured OC concentrations in the subsoil of this profile, while Fe does not. Only Ca appears to be important in the stabilisation of both top- and subsoil samples for this profile. It would, thus, appear that clay-cation-complexes are not important in the stabilisation of organic material in this profile. H exhibits a highly significant positive relationship with both illite (i.e. $r= 0.758$ ($p<0.05$), $r^2= 0.575$) and chlorite (i.e. $r= 0.814$ ($p<0.05$), $r^2= 0.663$). This is not unexpected as clay particles often interact with H^+ ions (Tan 1998). Such an association has been shown to lead to the decomposition of clay minerals. This may be the reason for the significant positive relationship between K and illite observed for this profile. The interaction of illite with H^+ ions may cause this mineral to destabilise, releasing its interlayer K cations into solution.

Table 5.33: Correlation Coefficients for % Cation Saturation and Clay Minerals Identified for the Königstein Profile

	Clay Mineral				
Cation	**Vermiculite**	**Mixed Layer**	**Illite**	**Chlorite**	**Kaolinite**
Na **- Correlation** **- Significance**	N= 7 0.039 0.935	N= 7 -0.024 0.960	N= 7 0.014 0.976	N= 7 -0.198 0.670	N= 7 -0.002 0.996
K **- Correlation** **- Significance**	N= 7 -0.180 0.700	N= 7 -0.414 0.356	N= 7 **0.719*** **0.069**	N= 7 -0.069 0.883	N= 7 -0.530 0.221
Mg **- Correlation** **- Significance**	N= 7 0.498 0.255	N= 7 0.440 0.324	N= 7 -0.288 0.530	N= 7 -0.769** 0.043	N= 7 0.351 0.440
Ca **- Correlation** **- Significance**	N= 7 0.554 0.197	N= 7 0.367 0.419	N= 7 -0.323 0.480	N= 7 -0.845** 0.017	N= 7 0.457 0.302
Fe **- Correlation** **- Significance**	N= 7 **0.742*** **0.056**	N= 7 0.336 0.462	N= 7 -0.369 0.415	N= 7 -0.878*** 0.009	N= 7 0.399 0.375
Mn **- Correlation** **- Significance**	N= 7 0.264 0.567	N= 7 **0.697*** **0.082**	N= 7 -0.555 0.196	N= 7 -0.621 0.136	N= 7 0.568 0.183
Al **- Correlation** **- Significance**	N= 7 -0.409 0.362	N= 7 -0.244 0.599	N= 7 0.067 0.887	N= 7 -0.681* 0.092	N= 7 -0.210 0.651
H **- Correlation** **- Significance**	N= 7 -0.626 0.133	N= 7 -0.549 0.202	N= 7 **0.758**** **0.048**	N= 7 **0.814**** **0.026**	N= 7 -0.751* 0.051

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.4.4 Profile 4: Geinsheim

As shown in Table 5.35, mixed layer illite/ smectite, illite and kaolinite exhibit significant positive relationships with Na and K. Specifically, mixed layer illite/smectite correlates strongly with the percent saturation of Na (i.e. 0.824 ($p< 0.01$), $r^2= 0.679$), while illite exhibits a positive relationship with K (i.e. $r= 0.821$ ($p< 0.01$), $r^2= 0.674$). Kaolinite also correlates with Na (i.e. $r= 0.691$ ($p< 0.05$), $r^2= 0.477$). Both K and Na, in turn, strongly correlate with both OC and N contents in a statistically significant manner and may, thus, serve as ‘bridges’ between organic matter and the above clay minerals. Na does not have much of a potential to protect organic matter, however, as this cation serves to disperse particles (Baldock and Nelson 2000). Similarly, K forms only weak bonds due to its valency and large ionic radius.

Table 5.34: Correlation Coefficients for % Cation Saturation and Clay Minerals Identified for the Geinsheim Profile

	Clay Mineral				
Cation	**Smectite**	**Mixed Layer**	**Illite**	**Chlorite**	**Kaolinite**
Na **- Correlation** **- Significance**	N= 9 -0.011 0.977	N= 9 **0.824***** **0.006**	N= 9 0.515 0.156	N= 9 -0.611* 0.081	N= 9 **0.691**** **0.039**
K **- Correlation** **- Significance**	N= 9 -0.255 0.507	N= 9 0.492 0.179	N= 9 **0.821***** **0.007**	N= 9 -0.319 0.403	N= 9 0.563 0.115
Mg **- Correlation** **- Significance**	N= 9 0.423 0.257	N= 9 -0.439 0.237	N= 9 -0.765** 0.016	N= 9 0.198 0.609	N= 9 -0.764** 0.017
Ca **- Correlation** **- Significance**	N= 9 -0.371 0.326	N= 9 0.045 0.908	N= 9 0.271 0.480	N= 9 0.104 0.790	N= 9 0.468 0.204

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

In sum, it appears as if the bridging mechanism between clay minerals and organic substances in the protection of organic matter does not play much of a role in the profiles under investigation. Of course, this conclusion assumes that significant positive statistical correlations between organic matter and cations and, in turn, cations and clay minerals, are a reliable indicator of such associations.

5.5 Specific Surface Area and OC and N Contents and C:N Ratios

The adsorption of organic substances on mineral surfaces has been a popular topic of investigation in attempts to clarify the mechanisms involved in the preservation of organic matter in both soils and sediments. It is not yet clear exactly what mechanisms are involved in adsorptive processes but the evidence suggests that the specific surface area (SSA) of a soil strongly influences the amount of organic matter which may be preserved. A positive correlation has been found between SSA and organic matter concentrations in several studies of both sediments and soils (Mayer 1994a, b; Keil et al. 1994a). These studies support the hypothesis of a ‘monolayer’ equivalent of organic carbon on mineral surfaces. The presence of minerals which have a large surface to volume ratio, notably clays, appear to be especially important in the stabilization of organic matter given the results presented in the literature. Statistical analyses of the relationship between SSA and the OC, N and C:N of samples from the sites under investigation are presented below. The five different silt and clay size fractions isolated from each bulk sample and their SSA and organic matter contents were the focus of analysis. The top- and subsoil samples from each profile were first analysed together to obtain an overview of potential patterns and trends (see Appendix M for an overview of scatter plots). As the A horizons and their associated organic matter inputs were expected to obscure possible relationships to some extent, they were then excluded from analysis to detect possible differences. Mayer (1994b), for instance, found that the organic carbon contents of topsoil samples were generally in excess of the ‘monolayer’ equivalent. Unlike for parameters measured for bulk soils, such as CEC, the number of samples allowed for a reliable analysis of subsoils in isolation.

Table 5.35: Correlation Coefficients for the SSA and OC, N and C:N of the Silt and Clay Size Fractions (< 63 µm) for the Whole Profile of Each Site

	Dependent Variable		
Site and Independent Variable	**OC**	**N**	**C:N**
Münden 1: **Specific Surface Area** **- Correlation** **- Significance**	N= 29 **-0.336*** **0.075**	N= 29 -0.042 0.827	N= 29 **-0.436**** **0.018**
Münden 2: **Specific Surface Area** **- Correlation** **- Significance**	N= 39 -0.165 0.317	N= 39 -0.114 0.489	N= 39 **-0.299*** **0.064**
Königstein: **Specific Surface Area** **- Correlation** **- Significance**	N= 33 0.014 0.938	N= 3 0.259 0.145	N= 33 -0.226 0.206
Geinsheim: **Specific Surface Area** **- Correlation** **- Significance**	N= 45 **0.459***** **0.002**	N= 45 0.199 0.191	N= 45 0.099 0.517
Frankfurter Stadtwald: **Specific Surface Area** **- Correlation** **- Significance**	N= 57 **-0.696***** **0.000**	N= 57 **-0.573***** **0.000**	N= 57 **-0.476***** **0.000**

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

Table 5.36: Correlation Coefficients for the SSA and OC, N and C:N of the Silt and Clay Size Fractions (<63 µm) for the Subsoils of Each Profile

	Dependent Variable		
Site and Independent Variable	**OC**	**N**	**C:N**
Münden 1: **Specific Surface Area** **- Correlation** **- Significance**	N= 18 0.131 0.603	N= 18 0.393 0.107	N= 17 0.082 0.754
Münden 2: **Specific Surface Area** **- Correlation** **- Significance**	N= 37 -0.067 0.694	N= 37 0.084 0.619	N= 37 -0.274 0.101
Königstein: **Specific Surface Area** **- Correlation** **- Significance**	N= 25 **0.395*** **0.049**	N= 25 **0.641**** **0.001**	N= 25 -0.207 0.320
Geinsheim: **Specific Surface Area** **- Correlation** **- Significance**	N= 30 **0.544***** **0.002**	N= 30 0.137 0.471	N= 30 0.119 0.530
Frankfurter Stadtwald: **Specific Surface Area** **- Correlation** **- Significance**	N= 39 **-0.309*** **0.055**	N= 39 -0.165 0.315	N= 39 **-0.514***** **0.001**

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

5.5.1 Profile 1: Münden 1

Both OC and the ratio of C:N correlate significantly with the SSA measured for the silt and clay size fractions isolated from the whole soil profile of the Münden 1 site (see Table 5.36 and Figures M.1, M.2 and M.3, Appendix M). These relationships are, however, negative ones (i.e. $r= -0.336$ ($p< 0.10$), $r^2= 0.113$ for OC and $r= -0.436$ ($p< 0.018$), $r^2= 0.190$ for C:N). This implies that there are decreases in the values of these variables with increases in SSA. For OC, we can assume that this observed relationship is due to the very large organic matter inputs to the top layers of this profile and its rapid decrease with depth. The OC loadings for the individual particle size fractions of the A horizon are in excess of that equivalent to a monolayer coating of organic matter on mineral surfaces (see Table 4.1, Section 4.5). Loadings then rapidly decrease, reaching levels below that for monolayer coverage. This yields a negative relationship between OC and SSA. The significant negative relationship for SSA and the ratio of C:N is expected, as the clay size fractions generally have the lowest ratios calculated for this profile (see Table C.3, Appendix C).

The above observed relationships for SSA and OC and the ratio of C:N become statistically insignificant when the A horizon is excluded from analysis (i.e. $p > 0.10$) (see Table 5.37). Overall, the results suggest that SSA is not an important variable in the stabilization of organic matter in the Münden 1 profile.

5.5.2 Profile 2: Münden 2

Similar to the Münden 1 profile, there is a significant negative relationship between SSA and the ratio of C:N when both the top- and subsoil samples are considered together (i.e. $r = -0.299$ ($p < 0.10$), $r^2 = 0.089$) (see Table 5.36 and Figures M.4, M.5 and M.6, Appendix M). This relationship is, however, rather weak. Further, this correlation is no longer statistically significant when the subsoil is analysed in isolation (see Table 5.37). Given the results for the Münden 2 profile, there appears to be no relationship between the OC content and SSA of silt and clay size separates. In fact, there appears to be a possible inverse relationship between SSA and OC for each fraction when considered separately. This is clearly an affect of depth, however. OC contents decline with depth, while SSA increases, with the highest values measured for samples isolated from the bottom of this profile. Again, we can assume that SSA is not an important factor in the preservation of organic matter in the Münden 2 profile.

5.5.3 Profile 3: Königstein

There are no observable relationships between SSA and OC, N and C:N for the silt and clay size fractions isolated from the Königstein profile when the top- and subsoils are analyzed together (see Table 5.36 and Figures M.7, M.8 and M.9, Appendix M). When the A horizon is eliminated from analysis, however, a positive relationship between OC content and SSA emerges, as shown in Table 5.37. This relationship is relatively weak, albeit statistically significant (i.e. $r = 0.395$ ($p < 0.05$), $r^2 = 0.156$). This relationship becomes stronger and more significant when samples taken from a depth of 10-25 cm are excluded from statistical analysis (i.e. $r = 0.675$ ($p < 0.01$), $r^2 = 0.455$) (not shown). This suggests that a positive relationship between SSA and OC is existent primarily for the lower depths of this soil.

Furthermore, there is a significant positive relationship between N content and SSA for the silt and clay size fractions from the subsoil of the Königstein profile, a relationship which is not observed for any of the other profiles. An r of 0.641 ($p < 0.01$, $r^2 = 0.411$) indicates that this relationship is even stronger than that observed for OC and SSA. This is confirmed by the raw results, which show that the finer particle size fractions with the largest SSA have the highest N contents (see Table C.9, Appendix C). In light of the results, it appears that SSA and sorptive processes of organic substances on mineral surfaces may play a role in the stabilization of carbon in the subsoil of the Königstein profile.

5.5.4 Profile 4: Geinsheim

As seen in Table 5.36, Geinsheim is the only profile where a significant positive relationship exists between SSA and OC contents when the A, B and C horizons are analysed together (i.e. $r= 0.459$ ($p< 0.01$), $r^2= 0.211$) (see Figures M.10, M.11 and M.12, Appendix M). This relationship becomes even stronger when only the subsoil is considered, with an r of 0.544 ($p< 0.01$, $r^2= 0.296$) (see Table 5.37). Of course, this is not an overly strong relationship in statistical terms but is highly significant. There is generally an increase in OC with corresponding increases in SSA, with the highest OC contents measured for the clay size fractions, with the exception of those samples from the bottom of the profile. At these depths, OC begins to decrease where groundwater influences become strong and the sand size fraction increasingly dominates the particle size distribution of bulk samples (see Table B.20, Appendix B). In terms of N contents and the ratio of C:N and SSA for the various size separates, there does not appear to be any relationship.

5.5.5 Profile 5: Frankfurter Stadtwald

All three variables, OC, N and C:N, correlate significantly with SSA for both the top- and subsoil samples from Frankfurter Stadtwald (see Table 5.36 and Figures M.13, M.14 and M.15, Appendix M). All correlations are, however, negative, with -0.696 ($p< 0.01$, $r^2= 0.479$) for OC, -0.573 ($p< 0.01$, 0.328) for N and -0.476 ($p< 0.01$, $r^2= 0.227$) for C:N. As shown in Table 5.37, these relationships become weaker and less significant with the exclusion of the A horizon (i.e. $r= -0.309$ ($p< 0.10$), $r^2= 0.095$, $r= -0.165$ ($p> 0.10$), $r^2= 0.027$ and $r= -0.514$ ($p< 0.01$), $r^2= 0.264$ for OC, N and C:N, respectively). For OC and N contents, we can assume that this is more the result of the large organic inputs to the A horizon and its declination with depth as opposed to an actual relationship with the area of mineral surfaces. Groundwater is an additional factor that must be considered in the interpretation of results. OC contents generally increase with decreases in the particle size fraction (i.e. with increases in SSA), reaching a maximum in the clay size fractions down to a depth of about 80 cm (see Table C.14, Appendix C). Below this depth, OC contents increase significantly and the silts, especially medium silts, typically contain the most OC. The ratio of C:N also increases at these depths, with the highest ratios associated with the coarse silt size fractions. This yields the highly significant negative relationship also observed between the ratio of C:N and SSA. The increase in both OC and the ratio of C:N at the bottom of the Frankfurter Stadtwald profile is most probably due to the virtual anaerobic conditions created at these depths because of the presence of groundwater for most of the year. This would prevent organic matter, either from roots or from organic particles being translocated from upper horizons downward as groundwater levels fluctuate through the course of the year, from being effectively mineralized by microorganisms. Once the data for the bottom of this profile is removed from the data set (i.e. 80+ cm), the significant negative relationship previously observed between SSA and OC content and the ratio of C:N disappears (not shown).

In sum, a positive relationship between OC and SSA of the silt and clay size fractions can only be determined for one profile, Geinsheim, when the top- and subsoils are analysed together. When the topsoil or A horizon is excluded from analysis, this relationship becomes stronger and a significant positive correlation between OC and SSA emerges for the Königstein profile. Although the observed relationships are not very strong they are statistically significant. In addition, there also appears to be a relatively strong positive relationship between N and SSA for the Königstein profile. These results suggest that observations made in the literature between organic matter and SSA are not applicable to all soils or sediments. We can state that there is an overemphasis on the importance of SSA and sorptive processes in the preservation of organic matter. Only in certain cases, does SSA seem to play a potential role in the stabilization of organic matter through adsorptive processes. To understand what mechanisms may help to protect soil organic material, an analysis of SSA is helpful but one must also look beyond and investigate other potential factors which may be operating in some soils but not in others. The role of oxides in stabilising soil organic matter will be the focus of the next section.

5.6 Dithionite- and Oxalate-Extractable Fe, Al, Mn and OC and N Contents and C:N Ratios

Although clay content has been the focus of past attempts to uncover the mechanisms of carbon sequestration in soils, the importance of oxides is becoming increasingly recognized.

The role of oxides in the stabilization of organic carbon has been emphasized for Andisols, which are weakly developed, volcanic soils with high organic carbon and amorphous oxide contents (Kimble et al. 2000). Amorphous Al and Fe oxides also appear to be involved in the complexation and translocation of organic compounds in Podzols (Chadwick and Graham 2000). In terms of other soil types, a number of studies in recent years have demonstrated the ability of oxides to readily adsorb and protect organic material (e.g. Boudot et al. 1988; Jardine et al. 1989, Jones and Edwards 1998; Kaiser and Zech 1999). As oxide minerals typically fall into the clay size fraction, their presence may be responsible for the relationship observed between clay size particle separates and organic carbon in many studies of the past.

The results of statistical analyses of the relationship between the presence of dithionite-extractable Fe (Fed) and oxalate-extractable Fe (Feo), Al (Alo) and Mn (Mno) and the OC and N contents of bulk soils are presented below. Emphasis is placed on the results for the entire soil profile for each respective site given the limited number of samples. Scatter plots of variables which display a significant positive relationship are displayed in Appendix N. Subsoils were analysed as well but must be interpreted with caution.

5.6.1 Profile 1: Münden 1

When both top- and subsoil samples are considered together, there are no observable significant correlations between Fed, Feo, Mno, Alo and the OC and N contents of bulk samples, as shown in Table 5.37. When samples from the top 20 cm of the profile are eliminated from the analysis, however, a highly significant positive correlation emerges between Feo and Alo and OC content (i.e. $r= 0.930$ ($p< 0.05$), $r^2= 0.965$ for Feo and $r= 0.960$ ($p< 0.05$), $r^2= 0.922$ for Alo) (see Table 5.38). This suggests that amorphous Fe and Al oxides may only be important in stabilising organic material at lower depths in this profile. Given that the sample size is only 4, however, when samples from the top 20 cm are excluded, this result is not overly reliable. Fed, which is a measure of both crystalline and amorphous Fe oxides, displays a strong negative correlation with the ratio of C:N (i.e. $r= -0.826$ ($p< 0.05$), $r^2= 0.682$). In contrast, Feo exhibits a strong positive relationship with the ratio of C:N, as reflected by an r of 0.905 ($p< 0.10$, $r^2= 0.819$). Feo occurs in the highest amounts in the top part of this profile, particularly between 5 and 20 cm (see Table H.1, Appendix H), where the ratio of C:N is at its highest.

Table 5.37: Correlation Coefficients Between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N= 7	N= 7	N= 6
- Correlation	-0.582	-0.117	**-0.826****
- Significance	0.170	0.802	**0.043**
Feo	N= 7	N= 7	N= 6
- Correlation	0.583	0.136	**0.905***
- Significance	0.170	0.771	**0.075**
Mno	N= 7	N= 7	N= 6
- Correlation	0.560	0.204	0.372
- Significance	0.191	0.660	0.468
Alo	N= 7	N= 7	N= 6
- Correlation	0.281	0.029	0.529
- Significance	0.541	0.950	0.280

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.38: Correlation Coefficients between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 1 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N=4	N=4	N=3
- Correlation	**-0.924***	0.198	**-0.998****
- Significance	**0.076**	0.802	**0.043**
Feo	N=4	N=4	N=3
- Correlation	**0.930***	-0.078	**0.991***
- Significance	**0.070**	0.922	**0.087**
Mno	N=4	N=4	N=3
- Correlation	0.793	-0.228	0.955
- Significance	0.207	0.772	0.191
Alo	N=4	N=4	N=3
- Correlation	**0.960****	-0.021	0.955
- Significance	**0.040**	0.979	0.191

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.6.2 Profile 2: Münden 2

Similar to Münden 1, there are no apparent significant positive relationships between Fed, Feo, Mno, Alo and OC and N contents when the entire profile is considered, as shown in Table 5.40.

Table 5.39: Correlation Coefficients Between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N= 9	N= 9	N= 9
- Correlation	-0.537	-0.478	**-0.763****
- Significance	0.136	0.193	**0.017**
Feo	N= 9	N= 9	N= 9
- Correlation	0.446	0.418	0.473
- Significance	0.229	0.263	0.198
Mno	N= 9	N= 9	N= 9
- Correlation	-0.548	-0.511	**-0.615***
- Significance	0.127	0.160	**0.078**
Alo	N= 9	N= 9	N= 9
- Correlation	-0.329	-0.344	0.140
- Significance	0.387	0.365	0.718

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Only when the A horizon is eliminated from analysis (i.e. the top 5 cm), does a positive relationship between the Alo and OC content of samples emerge, with an r of 0.637 ($p < 0.10$), $r^2 = 0.406$) (see Table 5.41). Alo also displays a significant positive relationship with N when the A horizon is excluded from analysis, with an r of 0.745 ($p < 0.05$, $r^2 = 0.555$), which is a slightly more significant, stronger correlation than that with OC. There is a significant negative correlation between Fed and the ratio of C:N (i.e. $r = -0.763$ ($p < 0.017$), $r^2 = 0.582$) when the whole profile is examined, to which the crystalline form of Fe is likely responsible. In subtracting Feo from Fed amounts, we see that the concentrations of crystalline forms of Fe increase progressively with depth, with the largest amounts being found at the bottom of the profile, where organic material occurs in highly degraded forms (see Table H.2, Appendix H). Mno negatively correlates with the ratio of C:N (i.e. $r = -0.615$ ($p < 0.10$), $r^2 = 0.378$). With the exception of the positive correlation between Alo and OC and N when the A horizon is eliminated from analysis, oxides generally do not appear to play an important role in the stabilization of organic compounds in the Münden 2 profile.

Table 5.40: Correlation Coefficients between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Münden 2 Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N=8	N=8	N=8
- Correlation	**-0.674**	-0.067	**-0.693***
- Significance	**0.067**	0.874	**0.057**
Feo	N=8	N=8	N=8
- Correlation	0.317	0.022	0.343
- Significance	0.444	0.959	0.405
Mno	N=8	N=8	N=8
- Correlation	-0.531	-0.181	-0.495
- Significance	0.176	0.669	0.212
Alo	N=8	N=8	N=8
- Correlation	**0.637***	**0.745****	0.407
- Significance	**0.090**	**0.034**	0.318

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.6.3 Profile 3: Königstein

In contrast to the Münden profiles, relationships between certain oxides and OC and N contents emerge for Königstein when both the top- and subsoil samples are analysed together (see Table 5.42). Specifically, Feo highly correlates with the OC (i.e. $r= 0.854$ ($p< 0.05$), $r^2= 0.729$) and N ($r= 0.830$ ($p< 0.05$), $r^2= 0.689$) contents of bulk samples, as well as with the ratio of C:N (i.e. $r= 0.928$ ($p< 0.01$), $r^2= 0.861$).

Table 5.41: Correlation Coefficients Between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N= 7	N= 7	N= 7
- Correlation	-0.561	-0.612	-0.377
- Significance	0.190	0.144	0.405
Feo	N= 7	N= 7	N= 7
- Correlation	**0.854****	**0.830****	**0.928*****
- Significance	**0.014**	**0.021**	**0.003**
Mno	N= 7	N= 7	N= 7
- Correlation	-0.185	-0.243	0.227
- Significance	0.691	0.600	0.624
Alo	N= 7	N= 7	N= 7
- Correlation	**0.676***	0.637	**0.911*****
- Significance	**0.095**	0.124	**0.004**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

This relationship becomes even stronger when the topsoil is excluded in analyses (see Table 5.43). Alo also exhibits a significant positive correlation with OC contents (i.e. r= 0.676 (p< 0.10), r^2= 0.457) when both top- and subsoils are considered together, albeit not as strong or significant as that between Feo and OC. Alo strongly correlates with the ratio of C:N (i.e. r= 0.911 (p< 0.01), r^2= 0.830), indicating that amorphous Al is also associated with fresh, less degraded forms of organic material.

Table 5.42: Correlation Coefficients between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Königstein Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N=5	N=5	N=5
- Correlation	-0.254	-0.487	0.061
- Significance	0.680	0.406	0.922
Feo	N=5	N=5	N=5
- Correlation	**0.979*** **	**0.802***	**0.914*** *
- Significance	**0.004**	**0.100**	**0.030**
Mno	N=5	N=5	N=5
- Correlation	0.846	0.613	**0.910*** *
- Significance	0.071	0.272	**0.032**
Alo	N=5	N=5	N=5
- Correlation	**0.982*** *	**0.803***	**0.911*** *
- Significance	**0.003**	**0.100**	**0.031**

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.6.4 Profile 4: Geinsheim

As displayed in Table 5.44, there is a highly significant correlation between Fed and both OC and N contents for bulk samples from the Geinsheim profile, with correlations of 0.760 (p< 0.05, r^2= 0.578) and 0.659 (p< 0.10, r^2= 0.434), respectively. Feo is even more strongly and significantly correlated with OC (i.e. r= 0.922 (p< 0.01), r^2= 0.850). In addition, Feo correlates with N contents (i.e. r= 0.790 (p< 0.01), r^2= 0.624) but not with the ratio of C:N. Alo also correlates with both OC and N, with r values of 0.720 (p< 0.05, r^2= 0.518) and 0.606 (p< 0.10, r^2= 0.367), respectively. These relationships become only slightly stronger if the topsoil is eliminated from the analysis (see Table 5.45). Overall, it would appear as if Al and especially Fe oxides play an important role in stabilizing organic material in this profile. A closer examination of the raw results also supports this supposition. For instance, there is an increase in OC and N at depths of 50-70 cm of this profile, compared to that for 25-50 cm (see Table C.10, Appendix C). This corresponds with an increase in Fe and Al oxides for these same depths (see Table H.4, Appendix H).

Table 5.43: Correlation Coefficients Between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N= 9	N= 9	N= 9
- Correlation	**0.760****	**0.659***	0.212
- Significance	**0.018**	**0.054**	0.584
Feo	N= 9	N= 9	N= 9
- Correlation	**0.922*****	**0.790****	0.129
- Significance	**0.000**	**0.010**	0.740
Mno	N= 9	N= 9	N= 9
- Correlation	0.210	0.363	-0.451
- Significance	0.588	0.337	0.224
Alo	N= 9	N= 9	N= 9
- Correlation	**0.720****	**0.606***	0.250
- Significance	**0.029**	**0.084**	0.516

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.44: Correlation Coefficients between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Geinsheim Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N=6	N=6	N=6
- Correlation	**0.754***	0.657	0.436
- Significance	**0.084**	0.156	0.388
Feo	N=6	N=6	N=6
- Correlation	**0.989*****	**0.832*****	0.407
- Significance	**0.000**	**0.000**	0.423
Mno	N=6	N=6	N=6
- Correlation	-0.159	-0.023	-0.356
- Significance	0.763	0.965	0.489
Alo	N=6	N=6	N=6
- Correlation	**0.736***	0.633	0.448
- Significance	**0.095**	0.177	0.373

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

5.6.5 Profile 5: Frankfurter Stadtwald

In the Frankfurter Stadtwald profile, primarily amorphous forms of Fe and Al appear to be associated with organic material, as reflected in the results displayed in Table 5.46. Specifically, Feo exhibits significant positive correlations of 0.706 ($p< 0.10$, $r^2= 0.498$) with

OC and 0.703 ($p < 0.10$, $r^2 = 0.494$) with N. Alo also correlates with both OC and N, with r values of 0.758 ($p < 0.05$, $r^2 = 0.575$) and 0.748 ($p < 0.10$, $r^2 = 0.560$), respectively. These results must be interpreted with caution, however, given the data points from the A horizon (see Figures N.13-N.16, Appendix N). These could be either outliers or indicators for the existence of a non-linear relationship between the examined variables. If the latter is true, we can expect that the strength of the relationships have been underestimated using the Pearson correlation coefficients calculated. The potential for samples from the A horizon to influence results is exhibited by the changes in the correlation coefficients when the topsoil is excluded from analysis. As shown in Table 5.47, the relationship between Feo and OC becomes stronger when the topsoil is excluded from analysis (i.e. r= 0.932 ($p < 0.10$), $r^2 = 0.869$), while that with N loses its statistical significance (i.e. $p > 0.10$). Similarly, Alo no longer correlates with OC and N in a significant manner. Fed positively correlates with OC in the subsoil of this profile (i.e. r= 0.920 ($p < 0.10$), $r^2 = 0.846$), while Mno exhibits a significant relationship with both OC and N (i.e. r= 0.967 ($p < 0.05$), $r^2 = 0.935$ and r= 0.913 ($p < 0.10$), $r^2 = 0.834$, respectively).

Table 5.45: Correlation Coefficients Between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Samples (<2 mm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed	N= 7	N= 7	N= 7
- Correlation	0.612	0.611	-0.193
- Significance	0.144	0.145	0.679
Feo	N= 7	N= 7	N= 7
- Correlation	**0.706***	**0.703***	-0.220
- Significance	**0.076**	**0.078**	0.635
Mno	N= 7	N= 7	N= 7
- Correlation	-0.231	-0.207	-0.330
- Significance	0.618	0.656	0.470
Alo	N= 7	N= 7	N= 7
- Correlation	**0.758****	**0.748***	-0.085
- Significance	**0.048**	**0.053**	0.857

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

Table 5.46: Correlation Coefficients between Fed, Feo, Mno and Alo and OC, N and C:N for Bulk Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile

	Dependent Variable		
Independent Variable	**OC**	**N**	**C:N**
Fed **- Correlation** **- Significance**	N=4 **0.920*** **0.080**	N=4 0.834 0.166	N=4 -0.217 0.783
Feo **- Correlation** **- Significance**	N=4 **0.932*** **0.068**	N=4 0.861 0.139	N=4 -0.260 0.740
Mno **- Correlation** **- Significance**	N=4 **0.967**** **0.033**	N=4 **0.913*** **0.087**	N=4 -0.367 0.633
Alo **- Correlation** **- Significance**	N=4 0.806 0.194	N=4 0.684 0.316	N=4 -0.006 0.994

***Correlation is at a level of 0.01 significant (2-sided)
**Correlation is at a level of 0.05 significant (2-sided)
*Correlation is at a level of 0.10 significant (2-sided)

In sum, the results here provide evidence that oxides, particularly amorphous forms, are important in stabilizing organic matter in the soils under investigation. Oxides seem to be especially significant in the profiles Königstein and Geinsheim. Both amorphous Fe and Al appear to be intimately associated with organic material in the Königstein and Geinsheim soils. Amorphous Fe seems to be even more important in stabilising organic matter in the Geinsheim profile though, as reflected by stronger correlations with OC and N. Both amorphous Al and Fe in the Münden 1 subsoil and amorphous Al in the Münden 2 B and C horizons appear to interact with organic material. Particularly for Münden 1, however, the results are not clear given the low sample number. In the Frankfurter Stadtwald profile, amorphous oxides also appear to stabilise organic matter.

Although oxides seem to be associated with OC and N to a greater extent compared to the clay minerals, they may not operate in isolation in the stabilization of organic matter. Similar to the cation ‘bridging’ mechanism, oxides also readily interact with clay minerals to form organo-mineral complexes which may lead to the protection of soil organic matter. As such, the relationship between oxides and clay minerals should also be examined to fully shed light on the mechanisms of organic carbon sequestration. These relationships are analysed in the next section.

5.7 Dithionite- and Oxalate-Extractable Fe, Al, Mn and Clay Minerals

To adequately assess the extent to which layer silicates may be associated with organic material, it is perhaps not sufficient to simply analyse the relationship between the OC and N contents and clay mineral composition as it is likely to be more complex. Oxides are strong aggregating agents in soils and are known to coat clay minerals (Schwertmann and Taylor 1989; Goldberg and Glaubig 1987; Goldberg 1989; Goldberg et al. 2000). In turn, oxides may be associated with organic matter, forming clay-oxide-organic complexes which help to stabilize organic materials. The relationship between oxides and the identified clay minerals should, thus, be analysed to investigate possible interactions. The results of statistical analyses of the relationships between the content of dithionite- and oxalate-extractable Fe, Mn and Al (i.e. Fed, Feo, Mno and Alo) and clay minerals for each of the soil profiles are presented below. Scatter plots of the variables which display a statistically significant positive relationship are shown in Appendix O.

5.7.1 Profile 1: Münden 1

Some clay minerals appear to be associated with oxides in the Münden 1 profile (see Table 5.48). Fed displays a highly significant positive correlation with both illite (i.e. $r= 0.923$ ($p< 0.01$), $r^2= 0.851$) and kaolinite (i.e. $r= 0.823$ ($p< 0.05$), $r^2= 0.677$). In contrast, Feo correlates negatively with these clay minerals, with r values of -0.908 ($p< 0.01$, $r^2= 0.824$) for illite and -0.785 ($p< 0.05$, $r^2= 0.616$) for kaolinite. This indicates that primarily crystalline Fe oxides are associated with these clay minerals in the Münden 1 profile. Amorphous Fe oxides are associated with vermiculite, as reflected by a strong positive correlation of 0.840 ($p< 0.05$, $r^2= 0.706$) between Feo and this mineral.

Mno exhibits a significant positive relationship with mixed layer minerals (i.e. $r= 0.761$ ($p< 0.05$), $r^2= 0.579$). In comparing the statistical analyses of the relationships between OC and N contents of bulk samples and oxides and clay minerals, there is little evidence which indicates the presence of clay mineral-oxide-organic complexes in this profile. When the entire profile is considered, Fed, Feo, Mno and Alo do not correlate with OC and N to any significant extent. Only when samples from the top 20 cm of the profile are eliminated, do Feo and Alo exhibit a strong positive relationship with OC. Of these oxides, only Feo is, in turn, positively correlated with vermiculite, an indicator of possible vermiculite-Feo-organic complexes in this soil. Due to the low number of samples when only the subsoil is considered for this profile, these results must be interpreted with care.

Table 5.47: Correlation Coefficients Between Fed, Feo, Mno and Alo and Clay Minerals for the Münden 1 Profile

	Fed	**Feo**	**Mno**	**Alo**
Vermiculite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.609	**0.840****	0.183	0.590
- Significance	0.147	**0.018**	0.694	0.163
Mixed Layer	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.611	0.304	**0.761****	0.416
- Significance	0.145	0.507	**0.047**	0.354
Illite	N= 7	N= 7	N= 7	N= 7
- Correlation	**0.923*****	-0.908***	-0.622	-0.804**
- Significance	**0.003**	0.005	0.136	0.029
Chlorite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.154	-0.179	0.238	0.418
- Significance	0.741	0.701	0.607	0.351
Kaolinite	N= 7	N= 7	N= 7	N= 7
- Correlation	**0.823****	-0.785**	-0.653	-0.756**
- Significance	**0.023**	0.036	0.112	0.049

***Correlation is statistically significant at a level of 0.01 (2-sided)

**Correlation is statistically significant at a level of 0.05 (2-sided)

*Correlation is statistically significant at a level of 0.10 (2-sided)

5.7.2 Profile 2: Münden 2

As shown in Table 5.49, Fed displays a relatively strong positive correlation with illite in the Münden 2 profile, with an r value of 0.752 ($p< 0.05$, $r^2= 0.566$). In terms of Fe oxides, the crystalline portion of Fed is most likely associated with this mineral, as Feo displays a significant negative correlation with illite (i.e. $r= -0.720$ ($p< 0.05$), $r^2= 0.518$). Mno also correlates significantly with illite, with an r of 0.717 ($p< 0.05$, $r^2= 0.514$). Alo correlates positively with chlorite (i.e. $r= 0.754$ ($p< 0.10$), $r^2= 0.569$). Overall, a number of positive correlations between the variables, notably Fed and Mno with illite and Alo with chlorite, indicate the possible existence of oxide coatings on these minerals. However, none of these variables positively correlate with the OC and N contents of bulk samples for the entire profile. Only when the A horizon (i.e. 0-5 cm) is excluded from analysis, does Alo exhibit a positive correlation with OC and N contents in a significant manner. Chlorite does not, however, positively correlate with OC in the Münden 2 soil. The presence of chlorite-Alo-organic complexes in the subsoil of this profile is, thus, unlikely.

Table 5.48: Correlation Coefficients Between Fed, Feo, Mno and Alo and Clay Minerals for the Münden 2 Profile

	Fed	**Feo**	**Mno**	**Alo**
Vermiculite	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.427	0.350	-0.280	0.406
- Significance	0.252	0.356	0.465	0.278
Mixed Layer	N= 9	N= 9	N= 9	N= 9
- Correlation	0.129	0.218	-0.146	-0.001
- Significance	0.741	0.573	0.709	0.998
Illite	N= 9	N= 9	N= 9	N= 9
- Correlation	**0.752****	-0.720**	**0.717****	-0.436
- Significance	**0.019**	0.029	**0.030**	0.241
Chlorite	N= 9	N= 9	N= 9	N= 9
- Correlation	0.152	0.016	0.049	**0.754****
- Significance	0.695	0.967	0.901	**0.019**
Kaolinite	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.225	0.044	-0.148	-0.666**
- Significance	0.560	0.911	0.703	0.049

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

5.7.3 Profile 3: Königstein

In terms of the Königstein profile, amorphous forms of Fe and Al oxides appear to be primarily associated with clay minerals (see Table 5.50). Alo and especially Feo correlate strongly with vermiculite, with r values of 0.809 ($p < 0.05$, $r^2 = 0.654$) and 0.909 ($p < 0.01$, $r^2 = 0.826$), respectively. Feo and Alo are also positively related to kaolinite, with correlations of 0.738 ($p < 0.10$, $r^2 = 0.545$) and 0.896 ($p < 0.01$, $r^2 = 0.803$), respectively. Amorphous Fe and Al appear to be associated with organic material, as reflected by the statistical results presented in the previous section, which show very strong positive correlations with the parameters OC and N and the ratio thereof. Both kaolinite and vermiculite also correlate with OC and N concentrations in this profile. In light of the evidence, we can assume that amorphous Fe and Al interact with vermiculite and kaolinite in this profile, which may serve as an important mechanism in the protection of organic matter.

Table 5.49: Correlation Coefficients Between Fed, Feo, Mno and Alo and Clay Minerals for the Königstein Profile

	Fed	**Feo**	**Mno**	**Alo**
Vermiculite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.542	**0.909*****	-0.163	**0.809****
- Significance	0.209	**0.005**	0.727	**0.028**
Mixed Layer	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.496	0.641	0.397	0.643
- Significance	0.258	0.121	0.378	0.119
Illite	N= 7	N= 7	N= 7	N= 7
- Correlation	0.323	-0.808**	-0.572	-0.946***
- Significance	0.480	0.028	0.180	0.001
Chlorite	N= 7	N= 7	N= 7	N= 7
- Correlation	0.580	-0.969***	0.050	-0.869**
- Significance	0.173	0.000	0.914	0.011
Kaolinite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.308	**0.738***	0.544	**0.896*****
- Significance	0.502	**0.058**	0.207	**0.006**

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

5.7.4 Profile 4: Geinsheim

As shown in Table 5.51, mixed layer illite/smectite exhibits a positive relationship with Feo (i.e. r= 0.649 (p< 0.10), r^2= 0.421). Both minerals also correlate with the OC and N contents of samples in this profile. Clay-oxide-organic complexes are, thus, likely to be present in this soil. Mno positively correlates with illite (i.e. r= 0.600 (p< 0.10), r^2= 0.360). Although illite displays a relatively strong positive correlation with N (r= 0.680 (p< 0.05), r^2= 0.462), neither this clay mineral nor Mno correlates with OC. The role of illite and Mno oxides in building complexes with organic material which leads to its protection is, hence, unlikely to be important.

Kaolinite contents correlate significantly with Alo (i.e. r= 0.644 (p< 0.10), r^2= 0.415), Fed (i.e. r= 0.672 (p< 0.05), r^2= 0.452) and especially Feo (i.e. r= 0.945 (p< 0.01), r^2= 0.893). Kaolinite also appears to be strongly associated with organic material, as reflected by a highly significant positive correlation with OC and N contents. Alo and Feo also significantly correlate with OC and N contents. Kaolinite is also predicted to form complexes with amorphous oxides, particularly with Fe oxides, in this profile which, in turn, are associated with organic matter.

Table 5.50: Correlation Coefficients Between Fed, Feo, Mno and Alo and Clay Minerals for the Geinsheim Profile

	Fed	**Feo**	**Mno**	**Alo**
Smectite	N= 9	N= 9	N= 9	N= 9
- Correlation	0.477	0.047	-0.302	0.536
- Significance	0.195	0.904	0.430	0.137
Mixed Layer	N= 9	N= 9	N= 9	N= 9
- Correlation	0.568	**0.649***	0.131	0.523
- Significance	0.111	**0.059**	0.737	0.148
Illite	N= 9	N= 9	N= 9	N= 9
- Correlation	0.214	0.517	**0.600***	0.156
- Significance	0.581	0.154	**0.088**	0.688
Chlorite	N= 9	N= 9	N= 9	N= 9
- Correlation	-0.913***	-0.701**	0.392	-0.898***
- Significance	0.001	0.035	0.296	0.001
Kaolinite	N= 9	N= 9	N= 9	N= 9
- Correlation	**0.672****	**0.945*****	0.158	**0.644***
- Significance	**0.047**	**0.000**	0.685	**0.061**

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

5.7.5 Profile 5: Frankfurter Stadtwald

For the Frankfurter Stadtwald profile, clay-oxide-organic complexes do not appear to be present, as shown in Table 5.52. Amorphous Fe and Al may be associated with organic matter, as reflected by strong, significant correlations between Feo and Alo and OC and N but the evidence is inconclusive given the data set (i.e. outliers). Feo and Alo do not correlate with any of the clay minerals identified in samples from the Frankfurter Stadtwald, which suggests that amorphous oxides bind only with organic matter.

To varying degrees, it would appear as if clay minerals interact with oxides, which are, in turn, associated with organic matter in most of the profiles investigated. The results particularly support the presence of strong relationships between amorphous Fe and Al oxides, clay minerals and organic matter in the Königstein and Geinsheim profiles. Vermiculite may form complexes with Fe in the Münden 1 subsoil. Given the low sample number though, no definite conclusions can be made. The role of clay mineral-oxide-organic complexes appears to be less important or nonexistent in the Münden 2 and Frankfurter Stadtwald profiles.

Table 5.51: Correlation Coefficients Between Fed, Feo, Mno and Alo and Clay Minerals for the Frankfurter Stadtwald Profile

	Fed	**Feo**	**Mno**	**Alo**
Smectite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.564	-0.564	0.094	-0.500
- Significance	0.187	0.187	0.841	0.253
Mixed Layer	N= 7	N= 7	N= 7	N= 7
- Correlation	0.570	0.570	0.586	0.505
- Significance	0.182	0.182	0.167	0.167
Illite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.017	-0.017	-0.479	0.000
- Significance	0.971	0.971	0.276	0.999
Chlorite	N= 7	N= 7	N= 7	N= 7
- Correlation	0.068	0.068	-0.140	-0.036
- Significance	0.885	0.885	0.764	0.940
Kaolinite	N= 7	N= 7	N= 7	N= 7
- Correlation	-0.193	-0.193	-0.202	-0.267
- Significance	0.679	0.679	0.664	0.563

***Correlation is statistically significant at a level of 0.01 (2-sided)
**Correlation is statistically significant at a level of 0.05 (2-sided)
*Correlation is statistically significant at a level of 0.10 (2-sided)

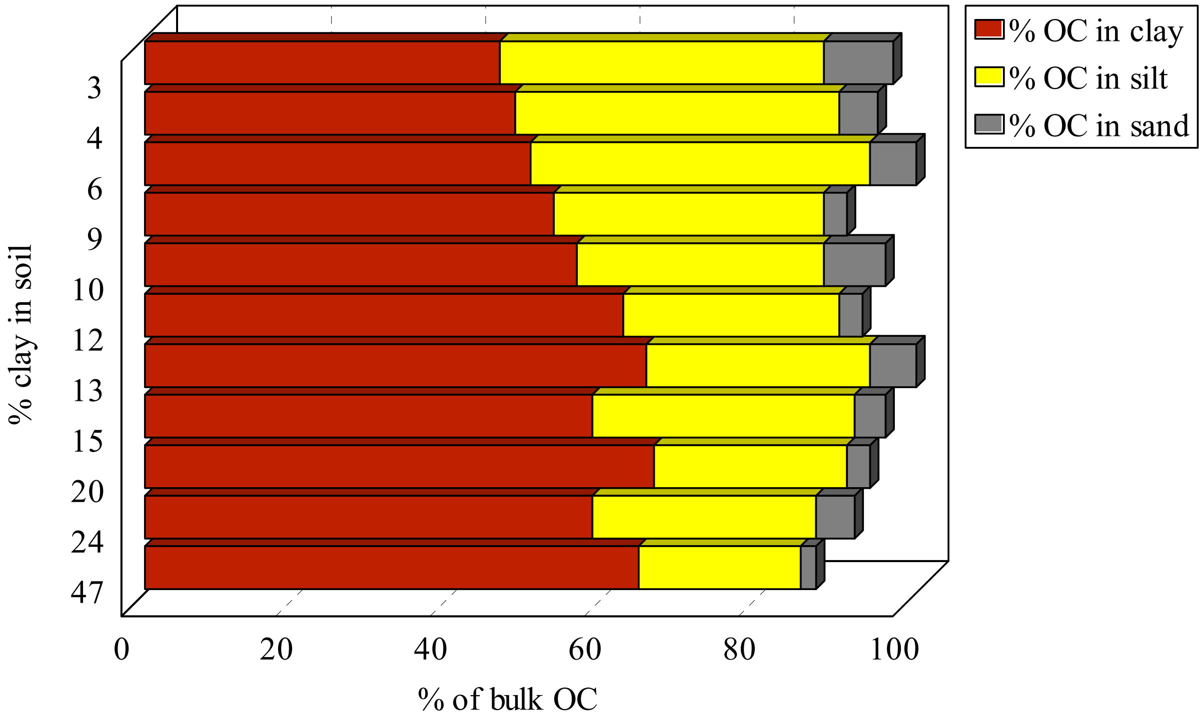
6. Discussion

According to the evidence presented in the literature, there appear to be a number of factors that influence the organic matter content in soils. Although some of this is contradictory, these factors include soil texture, notably the clay content of a soil, clay mineralogy and specific surface area (SSA). The latter is largely a function of mineralogy. In particular, sorptive processes appear to be significant in the preservation of soil organic material. The results presented here for the soils under investigation, however, do not to fully support or confirm observations which have been made in other studies. In fact, the evidence suggests that the importance of certain factors, especially clay content and specific surface area, have been overemphasized in the literature. Further, there seem to be differences between the soil profiles in terms of the mechanisms which may or may not play a role in the stabilization and preservation of organic matter. Care must, thus, be taken in making generalizations between soils. The next sections discuss the results of the various parameters measured in the context of the theoretical discussions and study results presented in the literature. This will be followed by a discourse regarding the potential of soils in general to stabilize and preserve organic carbon and their possible role in the global carbon cycle in the future.

6.1 Soil Texture, Particle Size Separates and the Dynamics of Organic Matter

The relationship between soil texture and organic matter dynamics has been a popular topic of investigation in the past (e.g. Turchenek and Oades 1979; Tiessen and Stewart 1983; Balesdent et al. 1988; Gregorich et al. 1988; Borchers and Perry 1992; Cambardella and Elliot 1993; Buyanovsky et al. 1994). Such studies have repeatedly demonstrated the existence of an inverse relationship between particle size separate and organic matter content, at least for temperate soils. Specifically, it has been found that the smaller particle size fractions, notably the fine silts and clays, often contain the greatest amounts of organic matter relative to the other size separates. For instance, between 35 and 70% of total soil organic carbon has been found to be associated with the clay size fraction (Feller and Beare 1997). For soils with >20% clay, it would appear that higher amounts of OC are associated with the clay size fraction relative to silt size separates, as the clay content of a soil increases. Figure 6.1, which is an adaptation from that presented in Christensen (1992), who compiled data from a variety of studies on Danish arable soils, nicely displays this relationship between the clay size fraction and OC content. Conversely, the OC and N enrichment of clay size particle separates has been found to be negatively related to the proportion of this fraction in bulk soil (Christensen 1992).

Figure 6.1: The Distribution of Organic Carbon among Size Separates in Bulk Soils from the A Horizons of a Number of Danish Arable Soils*



*Source: adapted from Christensen (1992)

In addition, clay size separates have often been demonstrated to contain greater amounts of nitrogen (Anderson et al. 1974; Christensen 1996, 2001). This nitrogen-enrichment, in turn, yields a low C:N ratio for these fine particle size fractions compared to silts and sands. This low ratio has often been interpreted as reflecting an organic component which is more recalcitrant and degraded due to microbial alteration (e.g. Amelung et al. 1998). Although a large amount of this material has been found to be the highly aliphatic products of degraded plant tissues, a significant portion of the organic compounds found in clays appear to be produced by microorganisms, which tend to be associated with this size fraction (Baldock et al. 1992; Christensen 2001). Of these microbial products, a proportion seems to be comprised of labile carbohydrates stabilized by an association with clay size particles. Turchenek and Oades (1979), for instance, calculated that the ratio of galactose + mannose/arabinose + xylose was higher for clays relative to other fractions in their study of four different soils, reflecting the presence of microbially synthesized polysaccharides. Recent evidence suggests that microbial products may dominate the organic component of the clay size fraction (Hedges and Oades 1997).

It has been pointed out that sorption of organic material on clay particle surfaces may, in fact, promote its mineralization (Guggenberger and Kaiser 2003). In a study conducted by Lünsdorf et al. (2000), biofilm which had formed on the surface of a water column overlying a sandy clay soil contaminated with PCBs was found to consist of clay aggregates comprised of bacteria, clay minerals, iron oxides and extracellular polysaccharides. Due to the affinity of clay minerals to bind with organic material, they propose that clay particles serve as “nutrient shuttles” for dissolved organic compounds passing through the water column. This “recruited” material, thus, becomes accessible to the bacteria, which are associated with the clay particles.

The results of this study also support the overwhelming evidence presented in the literature regarding the relationship between organic matter and various particle size fractions. First, an increase in organic carbon concentrations was generally observed with decreases in particle size. Fine silts were sometimes found to contain greater amounts of OC, such as in the Königstein profile down to a depth of about 25 cm. This is not extraordinary, however. OC concentrations have often been found to peak in the fine silt fraction, in addition to the clays (e.g. Turchenek and Oades 1979; Anderson et al. 1981). In spite of some deviations, the clay size fractions generally had the largest concentrations of OC in all profiles under investigation. Second, clays were typically found to contain the greatest amounts of N. A portion of the N associated with clays may be inorganic, due to an affinity of ammonium for clay surfaces (Moore and Reynolds 1997). Given the evidence in the literature though, this N enrichment would appear to reflect an association of microorganisms with this fraction. Third, the ratio of C:N declines with decreases in particle size, with the clay fractions typically having the lowest C:N ratios. There were, however, some exceptions to this. At a depth of 20-60 cm in the Münden 1 profile, for instance, clays actually had the highest ratio of C:N, indicative of less degraded forms of organic matter compared to the other size fractions. The reason for this is unclear but it may be a by-product of podzolization processes. In a study conducted by Schmidt et al. (2000) on the organic matter dynamics of a Podzol, the organic matter composition was found to vary between the A and B horizons. In the A horizon, the ratio of C:N decreased from the coarse to the fine particle size fractions, while the aliphatic nature of the organic matter increased. In the B horizon, the clay fraction was found to contain a significant amount of labile polysaccharides and lower amounts of aliphatic compounds (i.e. alkyl C), with a corresponding higher C:N ratio. This was attributed to the accumulation of iron and aluminium oxides and hydroxides in the clay fraction of this horizon, which readily bind organic compounds, leading to their stabilization and possible protection against mineralization. The Münden 1 profile, with its bleached eluvial horizon, also displays signs of podzolization. Concentrations of amorphous Fe and Al oxides peak at depths of 5-20 and 10-30, respectively. The higher ratios of C:N for the clay fractions observed could be related to such oxides and their potential to protect organic matter but the evidence is inconclusive. The role of oxides in the stabilization of organic matter in the profiles here will be discussed in Section 6.4.

Due to this apparent association between organic matter and clays, a positive correlation between the clay and OC content of soils has often been found (Ladd et al. 1985; Schimel et al. 1985); that is, soils with a higher clay content have often been shown to contain greater amounts of organic matter. In addition, clay content also appears to influence the turnover rate of organic carbon in soils. In their investigation of the rate of OC decomposition in the topsoil of several soils with varying clay content (5-42%), Ladd et al. (1985) found that the amount of OC remaining after eight years was proportional to clay content. Such results strongly suggest that clays have a stabilizing effect on soil organic matter.

Despite the fact that the clay size particle separates, in addition to fine silts, were generally found to contain the greatest amounts of OC, clay content only correlated with the OC concentrations of bulk samples for the profiles Königstein and Geinsheim (i.e. $r=0.843$ ($p<0.05$) and $r=0.807$ ($p<0.01$) for the two profiles, respectively). These correlations are rather high and indicate that clay content is a primary variable in controlling the variability observed in the OC contents of bulk samples for these two sites. Results for the other profiles, Münden 1 and 2 and Frankfurter Stadtwald, do not, however, exhibit a statistically significant relationship between the variables percent clay and OC content of bulk samples. For these profiles, the clays often contain the greatest amounts of OC. There are a number of deviations from this, however, where silts, notably fine silts, are associated with greater contents of organic material. In the Münden 1 profile, for instance, both fine silts and coarse clays contain the greatest amounts of OC down to a depth of about 30 cm. Below a depth of 85 cm in the Frankfurter Stadtwald profile, OC contents peak in the medium silt fraction. This is likely responsible for the lack of a statistically significant relationship between these two variables.

The same trends among profiles are also seen for N contents of bulk samples. Significant positive relationships between the N and clay content are observed only for Königstein and Geinsheim. These two variables correlated significantly for these two profiles, with r values of 0.812 ($p<0.05$) and 0.705 ($p<0.05$) for Königstein and Geinsheim, respectively. Clay content also correlated with the ratio of C:N for the Königstein profile (i.e. r= 0.954 ($p<0.01$)). This positive relationship suggests that greater amounts of 'fresh' forms of organic matter occur in association with increases in clay content for this profile. An inverse relationship would normally be expected, however, given that the clay fractions typically have a low ratio of C:N, as discussed above.

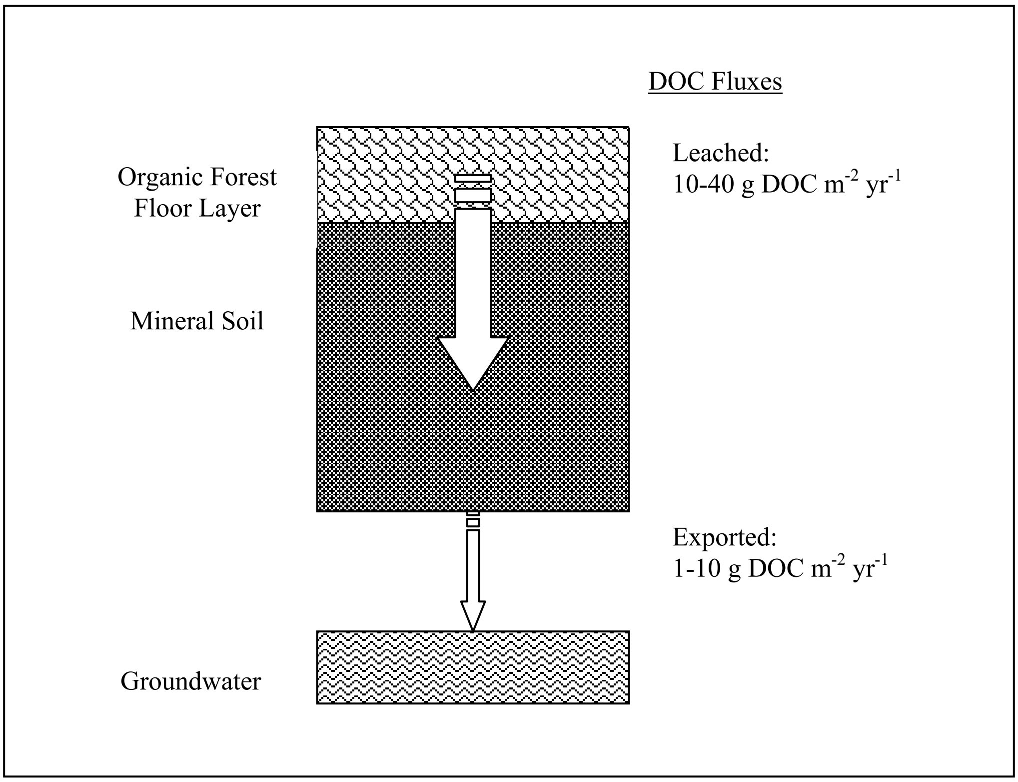
In terms of the Königstein profile, the results must be interpreted with caution as the observed significant relationships may be a product of the dynamics of particle size composition and OC and N contents with depth. Specifically, clay contents are highest in the A horizon and progressively decrease with depth, as do the OC and N contents of bulk samples. The observed relationships could, thus, simply be a result of these concomitant decreases with depth and do not necessarily indicate a causal relationship. We do not have this confounding factor in the Geinsheim profile though and can, therefore, assume that the observed statistical correlations are a reflection of actual relationships in reality.

Some researchers have even identified a difference in the OC content between the coarse and fine clay fractions. There is some evidence which suggests that the organic material in the coarse clay size fraction is recalcitrant and has a long turnover time, while that associated with fine clays is comprised of nutrient rich, labile substances (Tiessen and Stewart 1983; Anderson 1995). The organic matter in the fine clay fraction would normally have a high rate of turnover, but has been found to be stabilized and protected through its association with minerals. Assuming that the C:N ratios for what has been defined as "fine clays" for the purposes of this study are a reliable indicator of the degree of "freshness" of organic material in the samples, there is no evidence here to indicate that there are differences in the OC composition of coarse and fine clays (i.e. no observable differences in the ratio of C:N for these fractions). This is perhaps a positive result. In their investigation of four different soils, Turchenek and Oades (1979) also observed an enrichment of OC and N in the fine clay fractions of samples compared to the coarse clays but suggested that this may be artificial to some extent. Specifically, they point out that the presence of significantly greater amounts of OC and N in fine compared to coarse clays may be a result of the physical fractionation procedure used to isolate particle size separates, which may cause dissolved organic material to accumulate in the fine fraction.

Despite the observed correlations between the OC and clay content of bulk soils for Königstein and Geinsheim, comparisons of the OC concentrations of whole samples between all profiles portray a different story. In accordance with observations in the literature regarding the positive relationship between the clay and organic matter content of soils (see Christensen 1992), one would expect bulk soils from the profiles Geinsheim and Frankfurter Stadtwald to contain greater amounts of OC given their higher clay contents. This is clearly not the case (see Figure 4.1, Subsection 4.1.1). Although the Frankfurter Stadtwald profile exhibits greater amounts of OC in the top layers of this profile due to large vegetative inputs, concentrations rapidly decline with depth to levels similar to that found for the other profiles. For the Geinsheim profile, the OC content of samples in the A horizon is lower compared to the other sites. This is obviously due to the fact that very little vegetation grows at this site. At depths of 25-90 cm, OC contents are distinctly greater, however, than that found for bulk samples from similar depths at the other sites. OC contents at these depths may, therefore, be stabilized by clays to some extent. Below 90 cm in the Geinsheim profile, clay contents then decrease significantly, along with the OC concentrations of bulk samples. Care must be taken though in interpreting this perceived relationship. The soil at the Geinsheim site is likely to have an enormous self-mulching capacity, given the high smectite content. Hence, the seemingly stable OC content of samples with depth may be a result of organic matter being moved down the soil profile by the swelling and shrinking of clays.

Nonetheless, the Geinsheim profile does reflect the potential importance of OC preservation in subsoils. B and C soil profile horizons have often been neglected in studies of OC dynamics in the past. Their importance in terms of OC sequestration should not, however, be underestimated. Evidence in recent years suggests that subsoils contain a significant proportion of the organic carbon of a soil profile. Kaiser et al. (2002a) found, for instance, that 40-50% of the total soil OC of two soil profiles was situated in the subsoil. Figure 6.2, adapted from Guggenberger and Kaiser (2003) using information summarized by Michalzek et al. (2001), displays the DOC dynamics of forest soils. An approximate 10-40 g DOC m^{-2} yr^{-1} is leached from the organic surface layer to the mineral horizons, which amounts to about 10-25% of the total organic input to a soil. Most of this would appear to be sorbed or retained by the subsoil, as only 1-10 g DOC m^{-2} yr^{-1} has been estimated to be exported from the lowest profile depths.

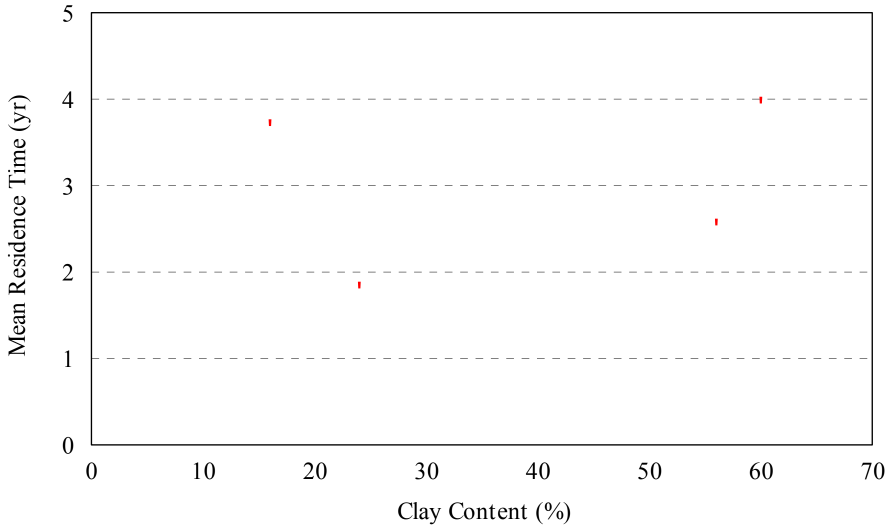
Figure 6.2: The Dynamics of Dissolved Organic Carbon (DOC) in Forest Soils*

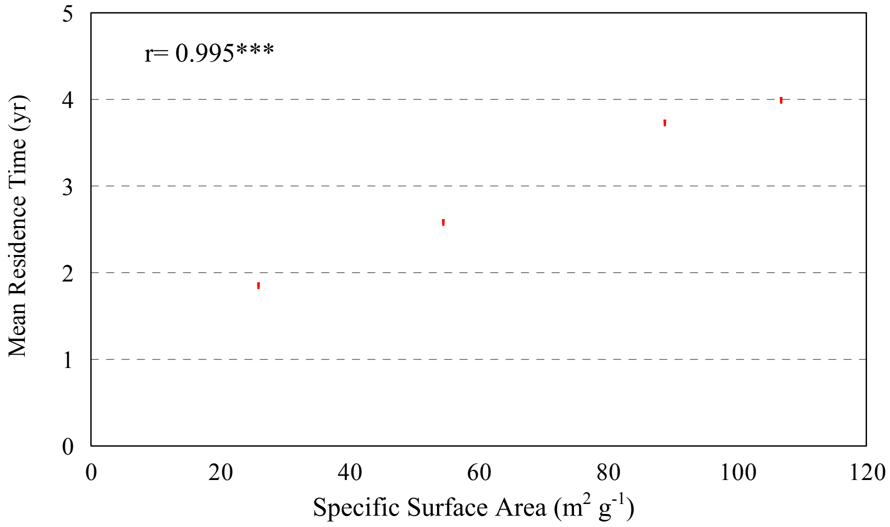


*Source: adapted from Guggenberger and Kaiser (2003)

Although the majority of profiles under investigation do not exhibit a relationship between clay and OC content, the results are not entirely in opposition to that found in the literature. There are a handful of studies that have been unable to find a relationship between these two variables. Mayer and Xing (2001), for example, found that clay content did not correlate significantly with the OC concentrations of most horizons in their study of various acidic soils in Massachusetts. Saggar et al. (1996), who studied the decomposition rates of ^{14}C-labelled ryegrass over a six year period in four different soils with varying clay content and clay mineralogy, also demonstrated that clay content did not correlate with the mean residence time of OC. Rather, they found that it was strongly correlated with the SSA of the soils under investigation, as illustrated in Figure 6.3. Of course, one could argue that a sample size of only four is not sufficient to equivocally establish a relationship between these variables. Low sample numbers are, however, common in soil sciences due to the work intensive nature of soil investigations. Nonetheless, given the evidence in the literature, we might conclude that the potential capacity for a soil to protect organic matter has less to do with clay content *per se* than with other factors such as clay mineralogy.

Figure 6.3: The Relationship between the Mean Residence Time of ^{14}C-Labelled Ryegrass and the Clay Content and Specific Surface Area of Four Different Soils*





*Source: adapted from Saggar et al. (1996)

6.2 Soil Organic Matter and the Role of Clay Mineralogy and Exchangeable Cations

The results regarding the relationship, or lack thereof, between clay content and organic matter concentrations in the profiles under investigation, indicate the need for a more critical examination of other factors, notably mineralogical composition, to shed light on the mechanisms of soil organic matter preservation. Sørensen (1972, 1975) was one of the first to illustrate the importance of clay mineralogy in the stabilization of soil OC. He demonstrated the capacity of a sandy soil to retain microbial by-products derived from ^{14}C-labelled substrates increased significantly with the addition of clay minerals. Further, he found differences in the ability of various clays to stabilize organic substrates. Specifically, small amounts of montmorillonite were shown to have a significant effect on the stabilization of newly formed metabolites, while kaolinite had little impact.

Numerous lab experiments have demonstrated that swelling 2:1 layer clay minerals, notably montmorillonite, have a large capacity to adsorb organic substances (see Greenland 1965a; Weiss 1969; Mortland 1970). This is particularly attributed to their large internal area, which makes up 80 to 95% of the total surface area of these minerals (see Table 6.1 for an overview of the SSA of various minerals). The SSA of montmorillonite ranges from 700 to 800 m^2 g^{-1} (Theng 1974). Most other clay minerals have relatively low SSAs such as kaolinite and illite, which have SSAs of 15 to 20 m^2 g^{-1} and 80 to 100 m^2 g^{-1}, respectively (Skopp 2000).

Table 6.1: The SSA of a Variety of Minerals Found in the Clay Size Fraction (<2 μm)

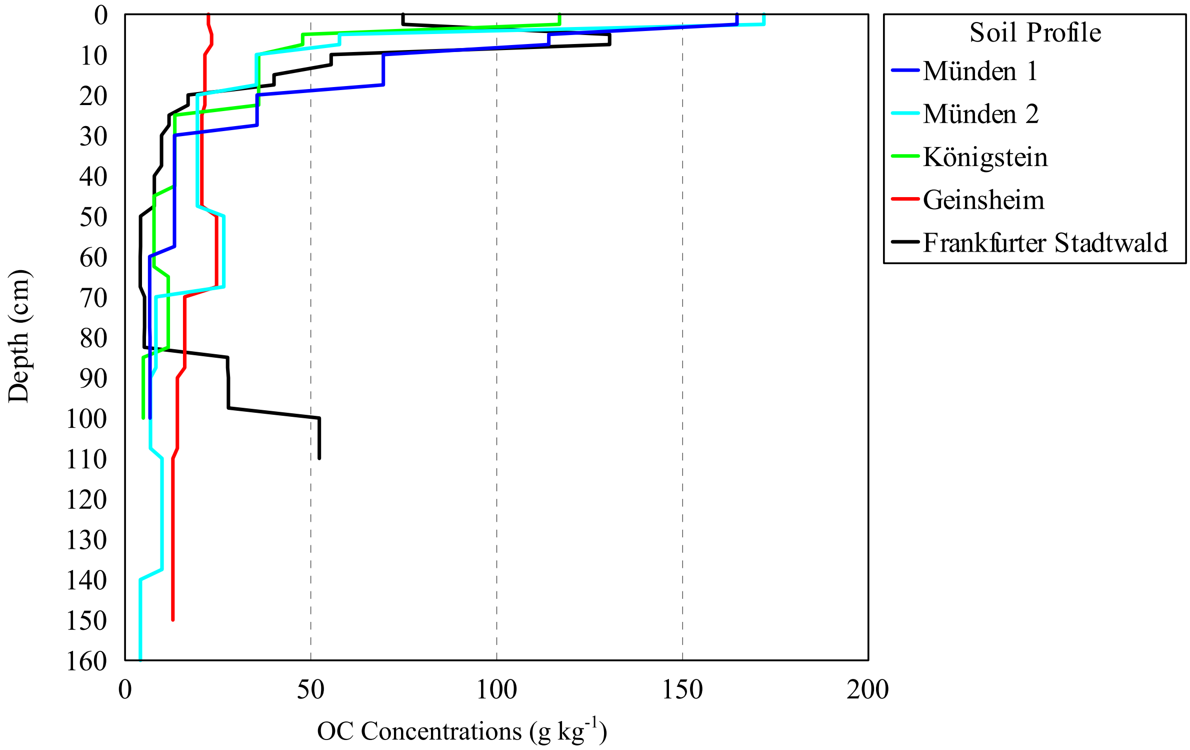
Mineral Component	**Total Specific Surface Area (m^2 g^{-1})**	**Internal Specific Surface Area (%)**
Kaolinite	15-20*	0
Illite	80-100*	0
Chlorite	160†	0
Smectite	600-800^{+}	80-90
Vermiculite	600-700^{+}	70
Crystalline Iron Oxides	50-200^{+}	0
Amorphous Iron Oxides	300-400*	0
Allophane	700-1100^{+}	0

(Sources: *Skopp (2000);† Theng et al. 1999; $^{+}$Kuntze et al. (1994))

Smectites have been shown to intercalate a large variety of neutral organic molecules, which essentially solvate the interlayer cations. The ease to which such molecules can be taken up by these minerals is evidenced by the fact that the use of ethylene glycol and glycerol is the most common method used to identify smectites (MacEwan and Wilson 1980; Moore and Reynolds 1997). Proteins also easily enter the interlayer spaces of smectites. For instance, montmorillonite has been shown to be able to adsorb up to 2.4 g protein g^{-1} (Greenland 1965a). Some anionic compounds have been reported to be adsorbed by sodium montmorillonite, most likely being associated with aluminium or aluminium oxides which are associated with the clay surface and act as a bridge. According to Greenland (1965a), however, the adsorption of organic polyanions have only been observed for external mineral surfaces and not in the interlayers. Theng (1982) contends that the intercalation of such compounds may occur at a low pH, which acts to suppress the negative charge of the polyanion.

Due to the amount of evidence which suggests the ease to which organic materials enter the interlayers of smectitic clays in the lab, it is often assumed that their presence in soils may serve to stabilize organic carbon. Vermiculite is also capable of intercalating organic materials but not to the same extent as smectites, as it has a higher surface charge density which prevents the interlayer space from expanding to any significant extent (Theng 1974; MacEwan and Wilson 1980; Moore and Reynolds 1997). In opposition to the results of lab experiments reported in the literature, there does not appear to be any evidence here which indicates that the intercalation of organic materials plays a role in the sequestration of carbon for the soils of concern. Those soils which contain significant amounts of smectites, notably Geinsheim and Frankfurter Stadtwald, do not have larger amounts of organic matter compared to the other profiles, as would be expected if these minerals intercalate organic materials. In terms of the Geinsheim profile, it is, of course, difficult to make comparisons to the other profiles, given the relatively low amounts of vegetative inputs to this profile. The profile Frankfurter Stadtwald contains comparatively greater amounts of organic carbon in the top layers of this profile. This is clearly due to the large amounts of plant litter deposited on this soil. This is evidenced by the fact that OC declines rapidly with depth, an indication that organic material is not protected from mineralization. Further, there are no major differences in the OC content of the clay size fractions between profiles, which is perhaps a better indicator of possible differences in clay mineralogical effects, as the relationships may be obscured when comparing bulk soils due to variations in clay content (see Figure 6.4). Clay size fractions isolated from the lower depths of the Geinsheim profile (i.e. about 70+ cm) do, however, contain somewhat greater amounts of OC. There are also significant increases in the OC content of clay size fractions from below 85 cm in the Frankfurter Stadtwald profile. However, this is unlikely due to any protective effects certain clay minerals may have in this profile. Rather, the anaerobic conditions induced by the presence of groundwater for most of the year at these depths is likely responsible for this observed increase in OC. Not surprisingly, there is no statistically significant relationship between the presence of smectites and the OC content of bulk samples for Geinsheim and Frankfurter Stadtwald. These results are similar to those reported by Wattel-Koekkoek et al. (2001), who investigated six smectitic and six kaolinitic soils and found that the carbon contents of the respective isolated clay fractions were not substantially different from one another.

Figure 6.4: OC Contents (g kg^{-1}) of Clay Size Separates (<2 mm) for all Sampled Profiles as a Function of Depth



Although swelling clays have been demonstrated to readily intercalate organic materials in the lab, there is very little evidence which supports its occurrence under natural soil conditions. As soil organic matter often carries a negative charge, it is not readily adsorbed on the negatively charged surfaces of clay minerals. The charge must be neutralized or suppressed or cations must be present to serve as a bridge between the clay surface and the organic material

(Greenland 1965b). In their investigation of an acid Podzol in New Zealand, Theng et al. (1986) demonstrated the presence of aliphatic material, likely a polymethylene chain, in the interlayers of smectitic clays. The presence of aliphatic material in the interlayers of smectites has also been confirmed by Schulten et al. (1996), who also studied the clay fraction of this Podzol from New Zealand. Schnitzer et al. (1988) found that about half of the organic matter associated with clay from the surface horizon of a Typic Haplorthod (i.e. Podzol) was composed of long-chain aliphatics, while the other half consisted of humic materials, especially fulvic acids. They contend that only fulvic materials are capable of entering the layers of clays under natural conditions as they are molecularly flexible, become neutral at a low pH and are water soluble, and, thus, can be transported through the soil profile. As aliphatics appear to be virtually water insoluble due to their hydrophobic character, and are rather inert, their association with clay minerals could only occur if they were transported and deposited on the mineral surface by fulvic acids. The intercalation of aliphatic material found in the Theng et al. (1986) and Schulten et al. (1996) studies could be explained by this transport mechanism. Apart from these three studies, there is no other known evidence which suggests that intercalation may play a role in the sequestration of organic materials under natural conditions.

In terms of the other clay minerals identified for the profiles and their relationship with organic matter, only a limited number appear to be associated with organic material in the profiles. Vermiculite appears to be associated with organic matter in the subsoil of the Münden 1 profile, as exhibited by a correlation of 0.916 ($p< 0.10$) with OC. This relationship is not very reliable though, as the sample number for the subsoil of this profile is low. This mineral also correlates with OC, as well as N, in the subsoil of the Königstein profile (i.e. $r= 0.855$ ($p< 0.10$) for OC and $r= 0.896$ ($p< 0.05$) for N). Kaolinite displays a strong relationship with OC in the Königstein subsoil (i.e. $r= 0.992$ ($p<0.01$)) and the Geinsheim profile (i.e. $r= 0.920$ ($p< 0.01$)). This mineral also highly correlates with N in the two profiles (i.e. $r= 0.824$ ($p< 0.10$) and $r= 0.745$ ($p< 0.05$) for Königstein and Geinsheim, respectively). Mixed layer illite/smectite correlates with both OC (i.e. $r= 0.644$ ($p< 0.10$)) and N (i.e. $r= 0.623$ ($p<0.10$)) in the Geinsheim profile. Illite also exhibits a positive relationship with the OC and N concentrations of samples from Frankfurter Stadtwald (i.e. $r= 0.515$ ($p< 0.10$) for OC and $r= 0.589$ ($p< 0.05$) for N). When the A horizon is eliminated from analysis, the relationships between illite and OC and N become even stronger and more significant (i.e. $r= 0.919$ ($p<0.01$) and $r= 0.851$ ($p< 0.01$), respectively). Strong positive correlations between OC and

N and chlorite (i.e. $r = 0.925$ ($p < 0.01$) for OC and $r = 0.932$ ($p < 0.01$) for N), as well as with kaolinite (i.e. $r = 0.839$ ($p < 0.01$) for OC and $r = 0.827$ ($p < 0.01$) for N) also emerge. It is unclear, however, whether these minerals actually help to protect or stabilize organic material in the Frankfurter Stadtwald profile. The increases in the OC and N contents of the fine particle size fractions at the bottom of this profile likely due to the presence of groundwater make it difficult to draw any reliable conclusions based on these results.

Kaolinite appears to play an especially important role in the stabilization of organic matter in the Königstein subsoil and Geinsheim profile. This is supported by the fact, for instance, that an increase in the OC concentrations of the clay size fractions between 65 and 85 cm in the Königstein profile corresponds to elevated levels of kaolinite at this same depth (see Table C.9, Appendix C and Table E.8, Appendix E). Oxide concentrations, in contrast, were not observed to increase at this depth. This result is interesting for this mineral is often assumed to be insignificant in interactions with organic material because of its neutral charge and small surface area. This mineral has broken edges though with exposed hydroxyl groups, which occupy as much as 20% of the total surface area (Theng 1974; Tan 1998). These edges can carry a positive charge under acidic conditions, making them capable of binding negatively charged organic materials. Other layer silicates may also have broken edges with reactive hydroxyl groups. As the other layer silicates have a larger permanent negative charge, however, the charge of these edges are effectively neutralized. Additionally, kaolinite has a large self-flocculation capacity (Tan 1998), which promotes the formation of aggregates which trap and protect organic materials. This mineral may, therefore, be significant in terms of its potential to protect organic material. The capacity of kaolinite to stabilize organic material has not received much attention in studies, the focus typically being on smectite. A couple of studies have demonstrated, however, that kaolinite has a greater potential to stabilize organic material than other clay minerals, notably illite. For instance, Jardine et al. (1989) demonstrated that kaolinite was able to adsorb 85% more organic material compared to illite in their investigation of two different soils. Similarly, Kaiser and Zech (2000) studied the sorption and desorption capacity of several mineral phases and found that kaolinite sorbed more dissolved organic material per surface area unit than did illite.

Apart from the exceptions discussed above, there do not appear to be any statistically significant positive relationships between the clay mineral composition and OC contents of samples from the profiles under investigation. We can not entirely assume, however, that clay minerals play an insignificant role in the stabilization of organic matter. First, the results may simply be a reflection of the method used for the quantification of clay mineral composition and not the lack of relationships which exist between the variables in reality. The use of XRD methods to quantify clay mineral amounts is well-known for its complications and difficulties (Moore and Reynolds 1997). This is, in part, due to interfering mineral reflections which may make it an onerous task to isolate peaks and their corresponding areas. For instance, first-order vermiculite and chlorite peaks often interfere with one another as they have similar d-spacing values (see Chen 1977). Caution must, therefore, be exercised in the interpretation of results. Second, clay minerals may have a protective effect on organic matter which does not show up in simple statistical estimates between two variables. Oxides are known to form coatings on clay minerals, which in turn, bind with organic materials (Cornejo and Hermosin 1996; Goldberg et al. 2000). These interactions help to flocculate soils and may form the basis of aggregates, which can be very effective in protecting organic matter from mineralization. The role of oxides and potential interactions with clay minerals in the soils of concern will be discussed in Section 6.4.

As previously discussed, organic material may also be bound to clay mineral surfaces through cations 'bridges'. Such clay mineral-cation-organic matter complexes may, in turn, form the basis of aggregates which may act to protect soil organic matter. Specifically, organic matter trapped within an aggregate will be physically protected from microbial attack. The importance of such a mechanism was demonstrated by Amelung and Zech (1996), who found that organic material within aggregates had a higher C:N ratio than that associated with the aggregate surface. It also had higher concentration of neutral sugars and lignin. Cations react readily with organic matter to from stable complexes (Oades 1988; Mortvedt 2000). As such, they are suspected to play a significant role in binding organic materials to the negatively charged surfaces of minerals. Oades (1988) emphasizes that the most important cations are Ca^{2+} and Mg^{2+} in alkaline soils and Al^{3+} and Fe^{3+} in ferrilitic and acidic soils. Ca^{2+} has been shown to protect organic matter from mineralization. In an unpublished study referred to in Oades (1988), for instance, soils with added calcium compounds retained higher amounts of ^{14}C-labelled organic material compared to the control soils. Cations such as Na^{+} and K^{+}, on the other hand, have a low capacity to protect organic matter. Sodium causes clays and organic materials to disperse, making organic compounds susceptible to decomposition (Tan 1998). It is not clear, however, whether the formation of Ca-organic matter linkages directly results in the protection of organic matter. It could be a result of the colloidal effects Ca^{2+} has on soils. Clay particles saturated with multivalent cations such as Ca^{2+} and Mg^{2+} tend to remain flocculated, reducing the exposure of organic material to microorganisms. Further, soils with large amounts of Ca^{2+} usually have greater amounts of organic matter as they tend to by more fertile due to their high base status and clay content (Oades 1988). This could, of course, have the potential to confound the effects of Ca^{+} linkages and interpretations regarding their potential to stabilize organic material. Some studies have demonstrated though that OC protection appears to be primarily due to the direct effects of the formation of Ca linkages with organic matter. In another study using ^{14}C-labelled fulvic acid, Theng (1976) demonstrated that the adsorption of organic material by montmorillonite was controlled by the type of exchangeable cation present at the clay mineral surface. Fulvic acid adsorption was shown to be most strongly influenced by the presence of Fe^{3+}.

For the profiles under investigation, exchangeable cations do not appear to be as intimately associated with organic matter as would be suggested in the literature. Ca (i.e. $r= 0.915$ ($p< 0.01$)) and Mg (i.e. $r= 0.673$ ($p< 0.10$)) saturation display highly significant strong correlations with the OC contents of bulk samples from Münden 1. These relationships become insignificant when the topsoil is excluded from analysis. Fe correlates with OC in the subsoil of this profile (i.e. $r= 0.928$ ($p<0.10$)). The sample number is, however, undesirable. For the Münden 2 subsoil, a significant positive relationship was observed between Al and OC and N (i.e. $r= 0.683$ ($p< 0.10$) for OC and $r= 0.625$ ($p<0.10$) for N). Mg, Ca, Fe and Mn saturation strongly correlate with OC in bulk samples from Königstein (i.e. $r= 0.936$ ($p< 0.01$), $r= 0.977$ ($p< 0.01$), $r= 0.943$ ($p< 0.01$) and $r= 0.750$ ($p< 0.10$), respectively). These cations also exhibited positive relationships with N contents in this profile (i.e. $r= 0.939$ ($p< 0.01$) for Mg, $r= 0.976$ ($p< 0.01$) for Ca, $r= 0.947$ ($p< 0.01$) for Fe and $r= 0.708$ ($p< 0.10$) for Mn). Again, these relationships become statistically insignificant when the A horizon is excluded from analysis. As such, they are unlikely to be involved in the stabilisation of organic matter in this profile. Only the relationships between Ca and OC and N remain essentially unchanged.

Given the low pH values of these three soil profiles however, any bonds which form between cations and organic compounds would be expected to be less strong compared to those formed in alkaline soils (Tan 1998). At a pH >7.0, both functional groups of organic compounds, carboxyl and phenolic-OH groups, are dissociated and chemically reactive. Thus, multiple bonds are possible between cations and organic materials at higher pH values. At low pH values, however, only the carboxyl groups may be dissociated, making only singular bonds possible. In light of this, potential associations between cations and organic matter in these profiles may not be as intimate or strong as those in the Geinsheim profile, which has a neutral to alkaline pH.

With respect to the Geinsheim profile, only Na and K correlate significantly with the measured OC contents of bulk soils (i.e. $r = 0.745$ ($p < 0.05$) for Na and $r = 0.777$ ($p < 0.10$) for K). These cations also correlate with N concentrations, with r values of 0.715 ($p < 0.05$) and 0.881 ($p < 0.01$) for Na and K, respectively. Na is particularly unlikely to have a protective effect on organic matter. The role of exchangeable cations in the stabilization of organic material appears to be minimal for the Geinsheim profile.

Of course, the existence of a positive relationship between the presence of certain cations and OC and N does not necessarily mean that organic matter is automatically protected. Cations such as Al, Ca and Mg reduce the repulsive forces between particles, allowing van der Waals forces to become effective, promoting particle interaction and aggregation (Oades 1988; Tan 1998). As already mentioned, cations may also form bridges between organic materials and minerals, an association which may form the basis of aggregates, which have a protective effect.

Analyses of the relationships between clay composition and exchangeable cations suggest that clay-cation-organic complexes only play a limited role in the profiles of concern. For the profile Münden 1, vermiculite correlates positively with Fe (i.e. $r = 0.847$ ($p<0.05$)), while mixed layer illite/smectite exhibits a positive relationship with Ca (i.e. $r = 0.883$ ($p<0.01$)). The former relationship would appear to be of greater importance, however, in terms of the protection of organic matter. Specifically, both vermiculite and Fe appear to be associated with OC in the subsoil of this profile. A significant relationship between Ca and OC only appears to exist when the whole soil profile is considered. The same holds true for mixed layer illite/smectite. Particularly in the latter case, the positive relationship appears to be the result of the data set (i.e. outliers). With respect to Münden 2, only illite and K appear to be associated with one another, with an r of 0.810 ($p < 0.01$). This association is expected, as K^+ ions are often fixed or entrapped in the intermicellar regions of clays (Tan 1998). They are normally inexchangeable but the presence of fulvic and humic acids, as well as an excess of

H^+ ions, promotes their release from the interlayers of this mineral. Neither K nor illite positively correlate with OC contents in the Münden 2 profile, however.

For the Königstein profile, Mn is positively related to mixed layer illite/smectite (i.e. $r= 0.697$ ($p< 0.10$)), while K correlates with illite (i.e. $r= 0.719$ ($p< 0.10$)). In addition, Fe exhibits a significant positive relationship with vermiculite (i.e. $r= 0.742$ ($p< 0.10$)). Of the cations, only Ca appears to be important in the stabilisation of organic matter in both the top- and subsoil of this profile. None of the clay minerals, however, correlate with this cation. In terms of the Geinsheim site, Na correlates with mixed layer illite/smectite (i.e. $r= 0.824$ ($p<0.01$)) and kaolinite (i.e. $r= 0.691$ ($p<0.05$)). K exhibits a significant relationship with illite (i.e. $r= 0.821$ ($p<0.01$)). Na and K correlate, in turn, with OC (i.e. $r= 0.745$ ($p<0.05$) for Na and 0.777 ($p<0.05$) for K), as well as with N (i.e. $r= 0.715$ ($p< 0.05$) for Na and $r= 0.881$ ($p< 0.01$) for K). As discussed above, however, K and Na ions are not likely to bind with clay minerals and organic compounds to form complexes that lead to the protection of organic matter in the Geinsheim profile.

Overall, it would appear as if clay minerals, even with the existence of cation linkages, may play a limited role in the stabilization of organic materials in the profiles under investigation. First, clay content correlates positively with OC for only two of the profiles, Königstein and Geinsheim. For the Königstein soil profile, however, it is not clear whether a relationship actually exists between these two variables, as clay content decreases with depth as do OC contents. The former may not necessarily be a causal agent of the latter. Second, the two profiles with significantly larger amounts of clays, notably Geinsheim and Frankfurter Stadtwald, do not exhibit greater concentrations of OC and N in bulk soils. This is despite the fact that large amounts of smectite minerals are present in these two profiles, which are predicted to retain more organic matter given their larger surface area and potential capacity to intercalate organic compounds. Third, there are only a limited number of clay minerals which exhibit significant positive correlations with OC and N contents in the profiles of concern. While smectite did not display a positive relationship with organic matter in the Geinsheim profile, kaolinite, for instance, was observed to correlate significantly with both the OC and N contents of samples. Kaolinite also appears to be associated with organic matter in the subsoil of the Königstein profile. In addition, the clay mineral vermiculite seems to be related to the OC contents of subsoil samples from the Münden 1 and Königstein profiles. The lack of a larger number of significant relationships which suggests that clay minerals play a protective role may, however, be due to the difficulties of quantifying the clay mineral composition of soils. Fourth, exchangeable cations, which have a high affinity for organic matter in the soil profiles, are positively related to only a few clay minerals, an indictor that clay minerals may be indirectly involved in the stabilization of organic material. In light of the above, the following sections will discuss other possible mechanisms that may be more important in the preservation of organic material in the soil profiles under investigation.

6.3 Specific Surface Area and Adsorptive Capacity

The results here suggest that other factors apart from the clay content or clay mineral composition *per se* are involved in the protection of OC in soils. The adsorption of organic compounds on mineral surfaces has become widely accepted as being the primary mechanism involved in OC sequestration. This has been particularly due to a number of studies on sedimentary systems which have established a significant relationship between specific surface area (SSA) and the OC concentration of marine sediments. Notably, Mayer (1994a, b), and his investigations of coastal marine sediments, has furthered the concept of mineral surface area as being the controlling mechanism in the preservation of organic material. Specifically, Mayer (1994a) found that surface area significantly correlated with the OC content of marine sediments and that this relationship approximates a “monolayer equivalent” (ME) coating of 0.86 mg OC m^{-2} on mineral surfaces. In other words, OC concentrations are equivalent to a monolayer coating of organic material on the surfaces of minerals. This relationship also seemed to hold regardless of the organic matter input amounts to sediments. He hypothesized that organic carbon is not distributed evenly over the mineral surface but is rather stabilized in the pores (i.e. mesopores) on surfaces that are too small for microorganisms and their enzymes to gain access. Kilbertus (1980) has suggested that bacteria are unable to access pores smaller than 3 µm. Hence, increases in surface roughness or number of small surface pores may result in greater amounts of organic material which could be protected.

The hypothesis that OC associated with sediments generally falls in the range of the ME has also been supported by Keil et al. (1994a). In their study of sediment samples from four different locations off the coast of Washington, OC contents were also found to be equivalent to a monolayer coating of organic materials on mineral surfaces. Further, Keil et al. (1994b) were also able to demonstrate that a large part of the adsorbed organic material is labile, being protected through the association with the mineral surface. Specifically, the organic matter, some of which had been dated as old as 500 years, was rapidly mineralised by microorganisms upon desorption. The strong association between organic material and mineral surfaces in sediments is evidenced by the fact that more than 90% of organic matter from a variety of depositional environments cannot be easily separated from the mineral matrix (Hedges and Keil 1995). Bergamaschi et al. (1997) also demonstrated the existence of a highly significant correlation between SSA and the OC contents of margin sediments from Peru. The ratio of OC to surface area was calculated, however, to be about 2.3 mg C m^{-2}, which is much higher than the ME determined by Mayer (1994a). The above results suggest that it is the amount of mineral surface area available for adsorption that determines organic carbon concentrations. In another study of marine sediments from continental slopes, virtually all the organic carbon appeared to be strongly associated with the mineral matrix (Ransom et al. 1998). While OC concentrations of samples from the one site fell within the range of a monolayer coating, samples from another site exhibited OC contents much higher than that predicted for a ME. Although the surface area of samples from the two sites was similar, the clay mineralogy differed. Specifically, the site with the high organic carbon concentrations had a rather high % of smectite (i.e. >21%), as well as metal oxyhydroxides, compared to the other site (i.e. <13% smectite). They conclude that mineralogy is, thus, more important than surface area in controlling OC contents. It should be mentioned though that SSA can not really be treated as being independent from mineralogy, as the former is largely determined by the latter. Additionally, their results should be interpreted with caution as they may be heavily influenced by the method used to measure surface area (i.e. BET method using N_2 adsorption). This method, which is the most commonly used to estimate the SSA of both soils and sediments, is potentially problematic when samples contain smectites. This arises from the fact that N_2 gas does not enter the interlayer of these minerals and can, thus, yield an underestimate of surface area unless some correction factor is used (Carter et al. 1986). This method has also been used by Mayer (1994a, 1994b; 1999) and Mayer and Xing (2001), as well as others such as Keil et al. (1994).

In addition to the existence of a ME coverage of organic material for sediments, it would appear that this relationship is also applicable to soils. In another study, Mayer (1994b) also investigated 21 A horizon soil samples and found that about half exhibited a ME relationship between OC concentrations and SSA. Soils that had OC contents in excess of the ME had either a high carbonate content, low pH or were poorly drained. Similarly, Mayer and Xing

(2001) found that the OC contents of topsoils for a number of acid soils in Massachusetts typically exceeded the ME level. The B and C horizons fell within this range, however. This suggests that subsoils may be a better indicator of the existence of a relationship between OC concentrations and SSA, as this may be obscured in an analysis of A horizons due to large litter inputs and/or low pH levels. Soil OC concentrations were also found to be related to SSA in a study conducted by Saggar et al. (1996), who monitored the decomposition of ^{14}C incorporated Ryegrass in four different soils with variable clay content and mineralogy over a 6 year period (see Figure 6.3). In an additional study, Kahle et al. (2002) investigated the relationship between a number of parameters and the OC dynamics of seven different loess-derived soils and found that surface area, as well as CEC, were the best predictors of OC contents (r^2=0.55 and r^2=0.54, respectively).

Given the evidence presented in the literature, it would, thus, appear that it is the amount of mineral surface area available for the adsorption of organic material which controls OC contents in both sediments and soils. Caution must be exercised, however, in the interpretation and application of the ME as coined by Mayer (1994a). As Mayer (1999) and Mayer and Xing (2001) point out, the term is misleading as organic matter is not likely to coat mineral surfaces evenly. In one study, Mayer (1999) calculated that marine sediments with low to moderate loadings of organic matter that fall within the ME had less than 22% of their surfaces covered. Rather, organic material is likely to be localised on mineral surfaces in patches that are thicker than a monolayer. The results of Ransom et al. (1997), who used transmission electromicroscopy (TEM) to investigate sediments from the northern California continental slope that fall within the monolayer equivalent, also support the likelihood that organic material is not present as evenly distributed coatings on particle surfaces, but is patchy in distribution and is primarily associated with clay-rich domains.

Calculated OC loadings for the mineral surfaces of the silt and clay size fractions isolated from the profiles under investigation here generally show an incompatibility, however, with that predicted using the ME hypothesis as proposed by Mayer (1994a) (see Tables 4.1 to 4.5, Section 4.5). Similar to the observations made by others (Mayer 1994b; Mayer and Xing 2001) regarding the A horizons of a variety of soils, the fine particle size fractions isolated from the Münden 1 and 2 and Königstein topsoils exhibit OC loadings that are in excess of that predicted for a ‘monolayer’ coating of organic material. We can assume that this is also related to the high litter inputs to these soils, combined with a low pH which serves to suppress microbial activity. OC loadings for the fine particle size fractions from the topsoil of the Frankfurter Stadtwald profile generally fell within the ME range, despite the large amount of organic matter being deposited on this soil. In contrast, OC loadings calculated for the Geinsheim profile fell below that predicted for “monolayer” coverage, a reflection of the little vegetation growing at this site. In the subsoil, depths which allow for a more reliable assessment of the existence of a ME level, the silt and clay fractions of all profiles displayed OC loadings substantially below that predicted by the “monolayer” hypothesis. The applicability of this hypothesis to the soil profiles of this study is, hence, questionable.

Statistical analyses of the SSA and OC contents of silt and clay size samples reveal that only Geinsheim exhibits a significant positive relationship between these two variables when both top- and subsoils are considered together (i.e. $r= 0.459$ ($p< 0.01$)). In other words, SSA is responsible for 21% of the variability in OC contents of this profile. There are also significant correlations between the SSA and OC content of the profiles Münden 1 and Frankfurter Stadtwald but these are negative, suggesting that there are decreasing OC contents with increases in SSA. The SSA measured for samples from Frankfurter Stadtwald also displays a negative relationship with N concentrations and the ratio of C:N. There is also a significant negative correlation between SSA and the ratio of C:N for the Münden 2 profile. These apparent inverse relationships between OC and N and SSA appear to be a product of the high organic carbon contents in the A horizons and its rapid decrease in the top layers of these profiles, as opposed to an actual relationship between SSA and OC and N. Clearly, the large organic inputs and the effects of depth obscure any real relationships which may exist in the A horizon and suggest the need to isolate top- and subsoils in the analysis of relationships between SSA and organic matter. This is supported by the fact that these negative relationships disappear when the topsoil (i.e. A horizon) is excluded from analysis. The negative correlations between SSA and the ratio of C:N for Münden 1 and 2 and Frankfurter Stadtwald are likely due to the fact that the clay size fractions with the highest SSAs are associated with the lowest ratios (Appendix C). These correlations also become insignificant when the A horizons are eliminated from analysis.

SSA also correlates with the OC concentrations measured for silt and clay size samples from Königstein when the B and C horizons are analysed in isolation from the topsoil. Specifically, a correlation of 0.395 ($p< 0.05$) was calculated for these two variables. This is not an overly strong relationship but it is significant and suggests that SSA determines the OC content of the Königstein subsoil to some extent. An r^2 of only 0.16 does imply though that there are other factors operating which are more important in regulating OC concentrations at this site. SSA is much more strongly related to the N content of Königstein samples, as displayed by a correlation of 0.641 ($p< 0.01$). This is not only twice as high as that between SSA and OC content, but is more significant. Given this value, SSA would appear to be a very important factor in controlling N concentrations, being responsible for about 41% of the variation in N between samples measured. The stronger relationship of SSA with N compared to OC may be due to an N enrichment of fine particle size fractions, notably clays, which also have the greatest measured SSAs. As previously discussed, microbial products have been observed to accumulate in the clay size fractions due to an association of microorgansisms with these particles (Turchenek and Oades 1979; Oades 1988; Christensen 1996, 2001; Feller and Beare 1997). It has been suggested, in fact, that there may be a group of biomacromolecules produced by microorganisms which are not readily detected with conventional analytical techniques, which are strongly bound to mineral surfaces (Oades 1995; Hedges and Oades 1997). The strength of the relationship between SSA and N compared to OC contents for the subsoil of the Königstein profile may, therefore, be a reflection of the tendency of microorganisms and their by-products to accumulate in the clay size fractions. In addition, the positive relationship observed between the SSA and OC contents for samples from the Geinsheim profile becomes somewhat stronger (i.e. $r= 0.544$ ($p< 0.01$)) when the A horizon is excluded from analysis. Although the relationship is not overly strong, the results suggest that SSA is a relatively important factor in controlling the OC contents of the Geinsheim soil.

In light of the results, surface area alone does not appear to be sufficient to account for the variability observed for OC concentrations in the soils under investigation. There are some soil studies discussed in the literature which support the findings presented here. Mayer and Xing (1999), for instance, found no correlation between SSA and OC in their investigation of acid soils in Massachusetts, although most soils fell within the ME level as defined by Mayer (1994a). In their investigation of near-shore sediments, Bock and Mayer (2000) suggest that sorptive processes may not be as important as microaggregate formation involving clays and interparticle porosity. Hassink et al. (1997) believe that the surface area of clays is not a good indicator for the potential of a clay or a soil to adsorb organic C and N based on their analyses of a number of soils from tropical and temperate regions. They demonstrated that the OC and N concentrations of the clay and silt fractions of the various soils were not significantly different from one another, despite differences in clay mineralogy.

6.4 Oxides and Soil Organic Matter: Interaction and the Role of Clays and Complex Formation

The role of oxides in a soil, especially amorphous Al and Fe oxides, in stabilising organic matter in soils has received greater attention in recent years due to a number of studies which have demonstrated a high affinity between these minerals and humic substances. The importance of amorphous metal oxides was demonstrated by Boudot et al. (1988), for instance, who investigated the organic matter dynamics in eight different Andosols. In a series of tracer experiments with labelled carbon and nitrogen, mineralization rates for both carbon and nitrogen were found to be reduced in the presence of oxalate-extractable Al (i.e. amorphous Al) and allophane. Oxalate-extractable Fe appeared to inhibit the mineralization of carbon but not nitrogen. Kaiser et al. (2002a) also showed that oxides are closely associated with organic matter. Specifically, they found that OC concentrations in the density fraction $d>$ 1.6 g cm^{-3} (i.e. clay fraction) of two forest profiles were strongly correlated to the content of oxalate- and dithionite-extractable Fe. In fact, Fe oxide concentrations were found to be an even better predictor of OC contents than the SSA of soil samples after destruction of organic material (i.e. an r^2 of 0.61). The results of Torn et al. (1997) radiocarbon analyses in their investigation of the relationship between soil mineralogy and soil organic carbon in volcanic soils also provided evidence of the greater importance of amorphous compared to crystalline minerals. They demonstrated that the abundance of non-crystalline minerals, including allophane, imogolite and ferrihydrite, accounted for >40% of the variation in organic C contents across all mineral horizons and soil orders. These amorphous minerals also appeared to strongly influence the turnover of organic matter.

In a handful of other studies, oxides have been demonstrated to have a much greater adsorptive potential for organic materials than clay minerals. Kaiser and Zech (1999), for instance, examined the adsorptive dynamics of dissolved organic carbon (DOC) on mineral surfaces and found that oxides (i.e. amorphous $Al(OH)_3$ gel and goethite) adsorbed more DOC than layer silicates (i.e. kaolinite and illite). Dissolved organic nitrogen displayed a similar adsorptive pattern as that for DOC. Organic nitrogen, which is largely part of larger organic macromolecules, is assumed to be sorbed passively with organic material. In addition, Jardine et al. (1989) showed that crystalline and noncrystalline Fe oxides and hydroxides in two different soils retained 50 to 70% of the total DOC adsorbed, while the rest was bound by other minerals in the clay size fraction, notably kaolinite. The greater potential of oxides to protect carbon compared to clay minerals is shown by Jones and Edwards (1998), who added

^{14}C-labelled citrate and glucose to four different soil substrates with contrasting mineralogy (i.e. a synthetic ferric hydroxide, an illite-mica, a poorly ordered kaolinite and a mixed clay with an illite/smectite, kaolinite and goethite). Of both carbon substrates, it was found that only citrate was adsorbed and not glucose, presumably due to its lack of charge. The greatest amount of citrate was adsorbed to the ferric hydroxide with 99%, while the kaolinite, mixed clay and illite-mica adsorbed 83%, 70% and 61%, respectively. In a desorption experiment, >90% of this citrate was desorbed for most of the soil substrates. In the case of ferric hydroxide, however, less than 40% of the citrate was desorbed. Jones and Edwards (1998) also found that very little of the citrate was decomposed by bacteria when it is associated with the ferric hydroxide (i.e. <1% in a 22 hr period), while as much as 65 and 25% was respired in the substrates containing illite-mica and kaolinite, respectively. This suggests that the oxide not only adsorbed more of the carbon substrate but that this association resulted in a greater stability and protection and longer residence time of the organic substance. The stability of such oxide-organic associations is also evidenced by the sorption-desorption experiments of Kaiser and Zech (1999) using goethite and $Al(OH)_3$. Humic materials were demonstrated to be strongly bound to the surfaces of these oxides, being only removed with difficulty. Further, rates of desorption decreased with increasingly longer periods of time between adsorption and desorption, which suggests that the longer the humic material is adsorbed, the stronger the stabilization over time.

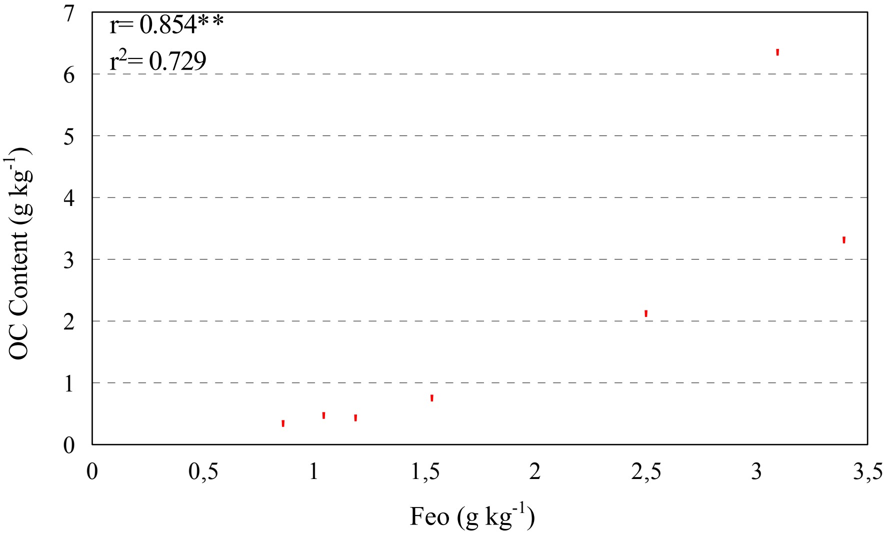
As exhibited by a variety of studies on humic substances in aqueous systems, the sorption of organic materials on oxide surfaces appears to be pH dependent (Tipping 1981; Davis and Gloor 1981; Davis 1982; Murphy et al. 1990; Gu et al. 1995, 1996a; Kaiser and Zech 1999). Specifically, the sorption of humic substances tends to increase with decreases in pH. As adsorption occurs, a corresponding increase in pH has often been demonstrated, which supports the hypothesis of the involvement of a ligand-exchange mechanism. Hence, it would appear that pH is also an important factor of consideration in judging the extent to which oxides may stabilize organic matter in soils. Further, it would appear that under favourable conditions, there is a virtual complete coverage of oxide surfaces and edge sites of aluminosilicates such as kaolinite, which suggests that the amount of surface area available for adsorption is a potential limiting factor (Davis 1982). Furthermore, these coatings appear to substantially alter the surface properties of the underlying mineral surface (i.e. high negative charges develop). The behaviour of minerals in natural systems are, thus, likely to be different from that predicted for ‘clean’ minerals in the laboratory. This is also supported by the results of Murphy et al. (1990) who found that the sorption of hydrophobic organic compounds (i.e. anthracene, dibenzothiophene, carbozole) on mineral surfaces (i.e. kaolinite, hematite and a clay fraction from a subsurface soil that contained both) was enhanced when the minerals were coated with humic materials. These coatings likely makes the surfaces more hydrophobic and capable of sorbing organic compounds. Other studies have also found that the high molecular weight, aromatic, acidic, hydrophobic fraction of dissolved humic substances appears to be preferentially adsorbed by mineral surfaces (e.g. Jardine et al. 1989, Gu et al. 1995, 1996a, b; Kaiser and Zech 1999), indicating processes of fractionation and competitive displacement of organic matter in its stabilisation. In contrast, low-molecular weight compounds appear to be rather mobile in soils, capable of mobilizing and transporting metals in acid soils such as Spodosols (Kaiser et al. 2002).

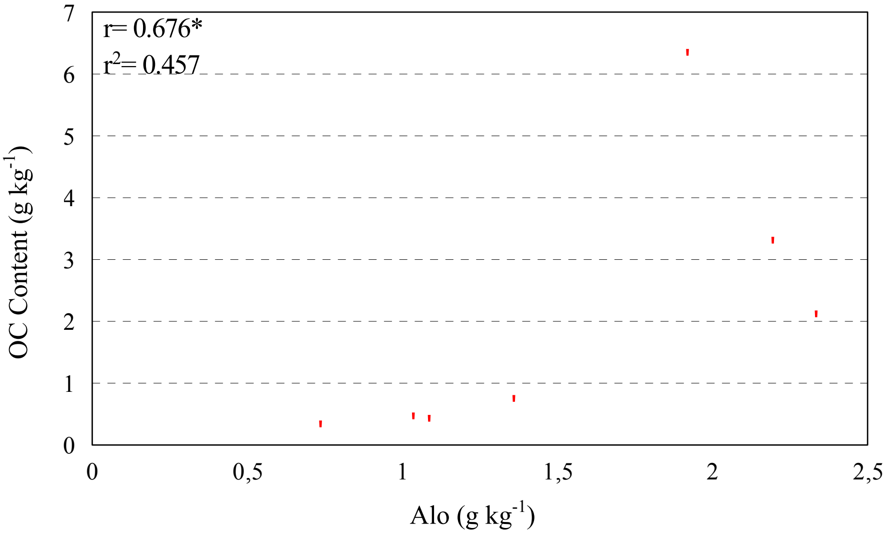
Statistical analyses of the relationship between the presence of oxides and the OC and N contents of the profiles under investigation in this study strongly support the evidence presented in the literature regarding the importance of oxides. Although there are no observable significant correlations between any of the oxides and the OC and N contents for bulk samples from Münden 1, some seemingly important relationships emerge when the A horizon is eliminated from analysis. Notably, amorphous Fe (Feo) and Al (Alo) oxides correlate strongly with the OC content of bulk samples (i.e. $r = 0.930$ ($p < 0.10$) and $r = 0.960$ ($p < 0.05$), respectively). This translates into r^2 values of 0.865 for Feo and 0.922 for Alo, which are very high and suggest that these oxides are important in controlling the OC contents in the subsoil of this profile. Given the limited number of samples analysed, however, when the A horizon is excluded from analysis, these results are not reliable. In addition, Feo positively correlates with the ratio of C:N when the entire profile is considered (i.e. $r= 0.905$ ($p<0.10$)). These Fe oxides are especially prevalent in the top layers of the profile, particularly at depths of 5-20 cm. Organic material at these depths has correspondingly higher ratios of C:N. Further, there is a strong negative correlation between Fed and the ratio of C:N, when results for the entire profile are analysed together (i.e. $r = -0.826$ ($p < 0.05$)). This implies that Fed is associated with older, more degraded forms of carbon. This may simply be a consequence of depth dependent factors, however. The crystalline component of Fed is clearly responsible for this relationship, which occurs in the highest concentrations at the bottom of the profile, where organic material has the lowest ratios of C:N.

Similar to Münden 1, certain oxides seem to only be positively related to the OC contents of bulk subsoil samples from Münden 2. When only the B and C horizons are considered, a significant positive correlation exists between Alo and OC (i.e. $r = 0.637$ ($p < 0.10$)). A $p < 0.10$ is not very optimal, however, and suggests caution should be exercised in the interpretation of this result. Alo is also strongly related to N contents (i.e. $r = 0.745$ ($p < 0.05$)) when the A horizon is excluded. Hence, amorphous Al oxides would appear to be associated with organic material that is enriched in OC and N in the subsoil of this profile. This relationship between Alo and N also supports observations in the literature that N has a high affinity for the surfaces of oxides (Boudot et al. 1988; Kaiser and Zech 2000). Unlike the other profiles, amorphous Fe does not appear to be associated with organic material in this profile to any significant extent. Fed is also negatively correlated with the ratio of C:N (i.e. $r = -0.763$ ($p < 0.05$)), of which the crystalline component again appears responsible. This relationship appears to be depth dependent, with the highest amounts of crystalline Fe present at the greatest profile depths where the ratios of C:N are at their lowest level.

For the Königstein profile, both Feo and Alo exhibit highly significant positive relationships with the OC content of bulk soils (i.e. $r = 0.854$ ($p < 0.05$) and $r = 0.676$ ($p < 0.10$), respectively). As shown in Figure 6.5, the presence of one outlier from the A horizon yields correlations that are somewhat biased. This is exhibited by the fact that the correlations become even stronger when the A horizon is excluded from analysis. Feo is also strongly correlated with N (i.e. $r = 0.830$ ($p < 0.05$)) and the ratio of C:N (i.e. $r = 0.928$ ($p < 0.01$)). Alo does not correlate significantly with N but is strongly related to the ratio of C:N (i.e. $r = 0.911$ ($p < 0.01$)). The results suggest that the relationship between amorphous Fe and Al and organic matter is stronger in the subsoil than in the topsoil. Statistical results are not overly reliable for this profile, however, when samples from the A horizon are excluded from analysis, due to the small sample size (i.e. $N = 5$ bulk samples from the B and C horizons).

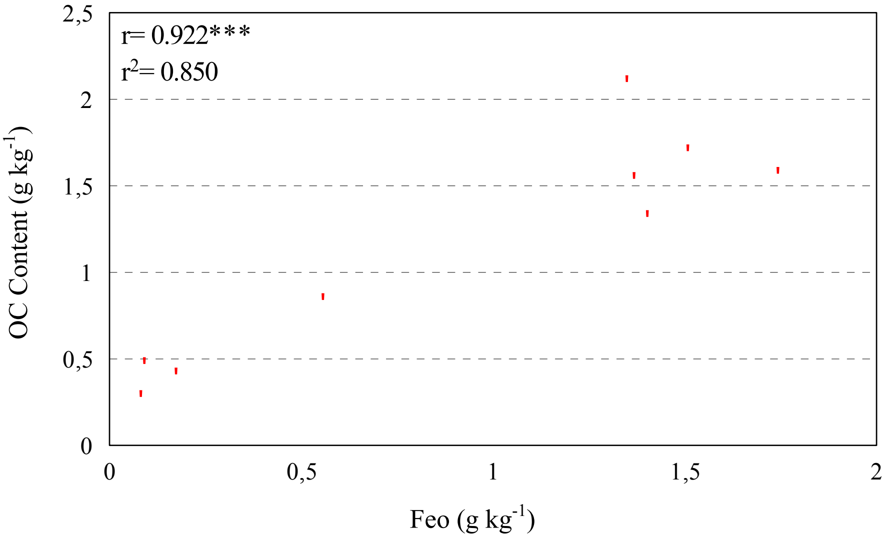
Figure 6.5: Relationships between OC and Feo and Alo for Bulk Samples (<2 mm) from the Königstein Profile

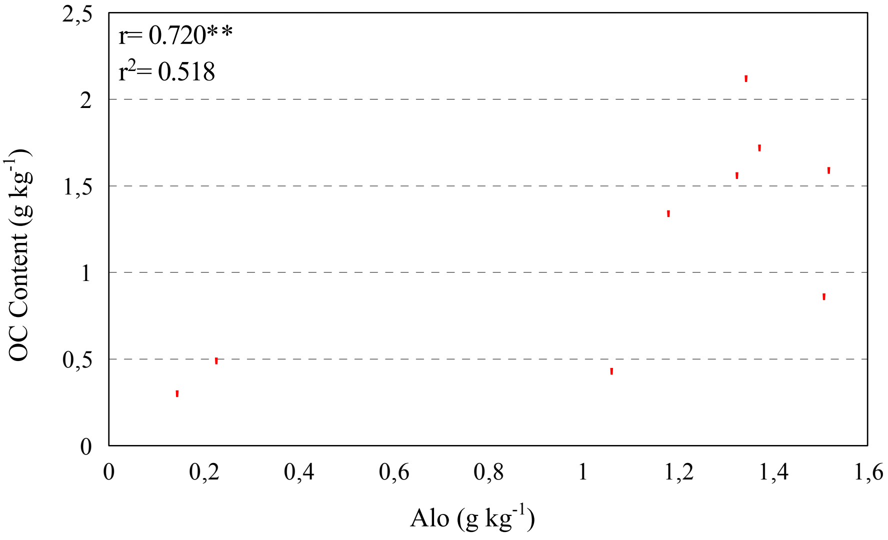




In terms of the Geinsheim profile, oxides also seem to play an important role in the stabilization of organic material. Alo is positively related to OC contents (i.e. r = 0.720 ($p < 0.05$)), as well as with N concentrations (i.e. r = 0.606 ($p < 0.10$)). The significance of the latter correlation is suboptimal, however, and can only be used to draw tentative conclusions. The relationships between Feo and OC and N are highly significant and indicate a strong association between these variables for this profile (i.e. r = 0.922 ($p < 0.01$) for OC and r = 0.790 ($p < 0.01$) for N). If the A horizon is excluded from the analysis, these relationships become only slightly stronger. It would appear as if amorphous Fe has a higher affinity for organic material enriched in OC and N than the Al oxides in this soil (see Figure 6.6). The positive correlations observed between SSA and the OC contents of samples from both profiles is perhaps, in large part, a reflection of the importance of the sorption of organic material on oxides in these soils.

Figure 6.6: Relationships between OC and Feo and Alo for Bulk Samples (<2 mm) from the Geinsheim Profile





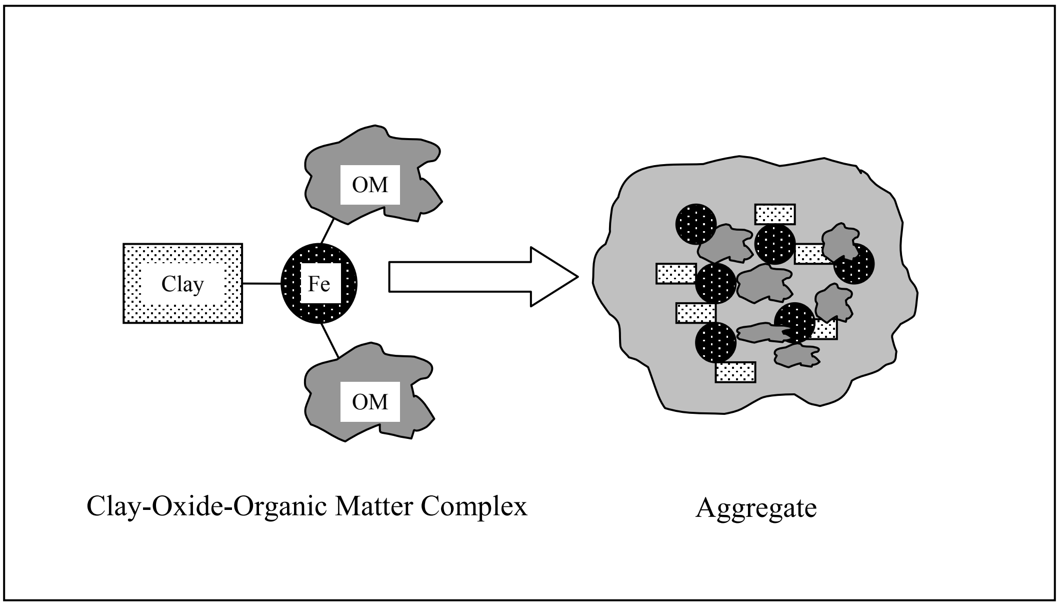
Highly significant positive correlations were calculated for Feo and Alo and OC and N for the Frankfurter Stadtwald profile. As shown in Figures N.13-N.16, Appendix N, there is an extreme curvature though in the data points. The data points from the A horizon could be outliers. However, this curvature is more likely to be indicative of a non-linear relationship between the variables, reflecting a higher saturation of oxide surfaces in topsoil. Groundwater influences in the subsoil of this profile could disrupt associations between Fe oxides and organic material, given the fact that these oxides are reduced and mobilized under anaerobic conditions (Schwertmann & Taylor, 1989). Given that Pearson correlation coefficients were used, we can assume that the correlations between the variables have been underestimated.

Overall, oxides appear to play an especially important role in stabilizing organic matter in most profiles to varying degrees, particularly in the Königstein and Geinsheim soils. Both Feo and Alo display strong relationships with OC in samples from the Königstein and Geinsheim sites. Amorphous Fe would appear to have a greater affinity for organic matter in the Geinsheim profile compared to Al oxides. This contrasts with the results of Boudot et al. (1988), who demonstrated that OC and N have a stronger affinity for Alo than Feo. Both Feo and Alo also strongly correlate with the OC contents of samples from the Münden 1 profile when the A horizon is not considered. Amorphous Al oxides appear to be associated with organic material in the Münden 2 subsoil.

Regardless of whether Al or Fe oxides are more important, the results strongly indicate that the amorphous or non-crystalline oxides have a larger capacity to bind with and potentially protect organic materials. As previously mentioned, Torn et al. (1997) also demonstrated the importance of amorphous materials in controlling organic carbon contents in their analysis of volcanic soils. They suggest, however, that the ability of non-crystalline minerals to stabilize carbon will decrease over time as these minerals become more crystalline and stable. It should be noted though that the adsorption of organic substances on non-crystalline oxides can suppress crystallisation (Cornell and Schwertmann 1979; Violante et al. 2002). Thus, their adsorptive capacities may not necessarily be reduced over time.

In comparing the statistical results of the relationships between organic matter and clay minerals and oxides, this study has demonstrated that oxides have a greater affinity for and capacity to stabilize organic matter in the soils of concern. As mentioned though, the absence of a relationship between clay mineral composition and organic matter content does not necessarily mean that clay minerals do not play a role. Together with oxides, clay minerals may form complexes and aggregates which serve to protect soil organic materials (see Figure 6.7 for a conceptual model of such a complex and how it aggregates may form). It is well known that oxides readily form coatings on clay mineral surfaces, which, in turn, bind organic materials. There is evidence which indicates, for instance, that iron oxides readily adsorb on kaolinite surfaces (Schwertmann and Taylor 1989). This causes a cementation effect, whereby soil particles are strongly aggregated, leading to the formation of concretions and crusts. In opposition to that which is often said in the literature though, Al oxides may be more important in aggregate formation and stability (Goldberg and Glaubig 1987; Goldberg 1989). This is due, in part, to their platy or flat structure which is better suited to binding particles together than the spherical structure of Fe oxides. Regardless of which oxide is more important though, both Al and Fe oxides serve to stabilize clay minerals and promote the formation of aggregates by encouraging flocculation and reducing clay dispersion and swelling (Goldberg 1989).

Figure 6.7: Conceptual Model of a Clay-Oxide-Organic Matter (OM) Complex and How Aggregates may Form



The formation of oxide coatings is made possible by the positive charge that most oxides carry under acidic soil conditions. Hydroxyl groups on the edges of oxides, hydroxides and the aluminosilicates imogolite and allophane, as well as kaolinite, are the most abundant and reactive surfaces in soils. Most of these surface hydroxyl groups are amphoteric; that is, they have a positive charge at low pH and a negative charge at high pH. If there is a surplus of H^+ in the system, these ions will attach themselves to the mineral surface which results in a positive charge, whereas an excess of OH^- will result in a negative charge. Fe and Al oxides generally undergo a surface charge reversal in the range of pH 7 to 9 (Goldberg et al. 2000). Hence, Fe and Al oxides are likely to carry a positive charge in the soils under investigation. Table 6.2 displays representative points of zero point charge (ZPC) for a variety of common oxides found in soils.

Table 6.2: Points of Zero Point Charge for a Variety of Common Oxides in Soils

Oxide	**Zero Point Charge***
Goethite	8.8
Hematite	8.5
Amorphous Fe	8.0
Amorphous Al	9.3
Gibbsite	9.8
Bayerite	9.2
Boehmite	9.4

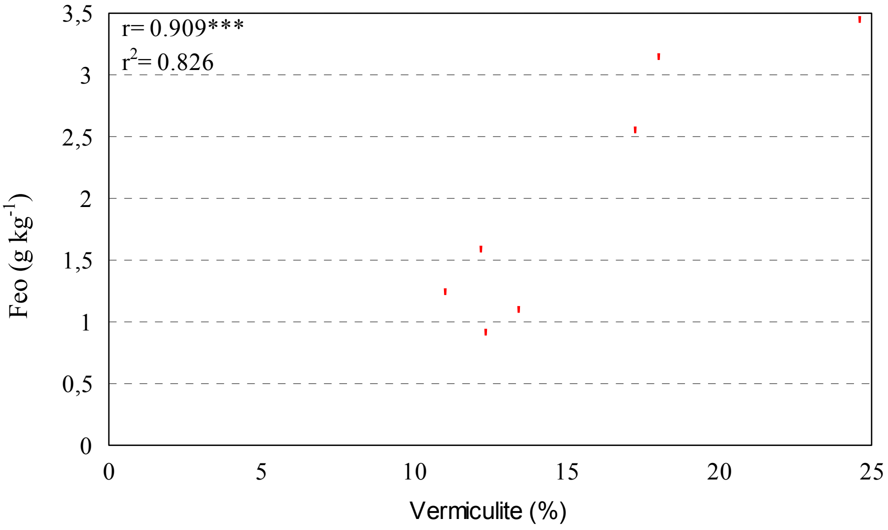
*determined using electrophoresis

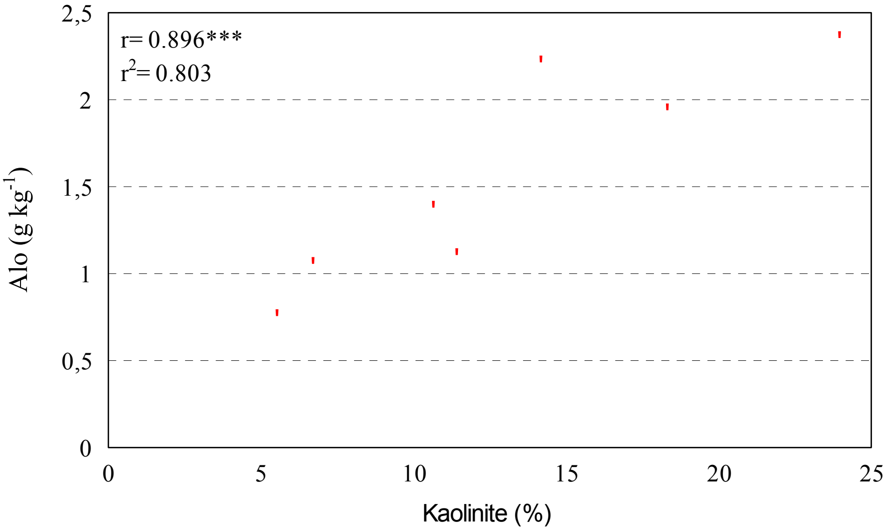
(Source: from Goldberg et al. 2000)

We can expect that the oxides present in the Münden and Königstein and Frankfurter Stadtwald profiles are more reactive and have a greater affinity for organic material and clay minerals than that in the Geinsheim profile, as these profiles are considerably more acidic (i.e. < pH 5.0). As shown by some studies (e.g. Tipping 1981; Davis and Gloor 1981; Murphy et al. 1990), the adsorption of organic compounds on oxide surfaces appears to increase with decreases in pH. A reduced adsorption of organic material has been shown, however, to already occur in the pH range of about 6 to 8, values which approach the ZPC of most Al and Fe oxides. Oxides may, thus, be less reactive in the Geinsheim profile as the pH also falls within this range.

The statistical results suggest that oxides and clay minerals interact to some extent to form complexes with organic materials in the soil profiles. In particular, oxides appear to be strongly associated with clay minerals in the profiles Königstein and Geinsheim. In the Königstein profile, Feo and Alo, both of which exhibit strong relationships with OC, highly correlate with vermiculite (i.e. $r = 0.909$ ($p < 0.01$) for Feo and $r = 0.809$ ($p < 0.05$) for Alo). Feo and Alo are also strongly related to kaolinite (i.e. $r= 0.738$ ($p<0.10$) and 0.896 ($p<0.01$) for Feo and Alo, respectively) (see Figure 6.8 for an example of the scatter plots for these variables).

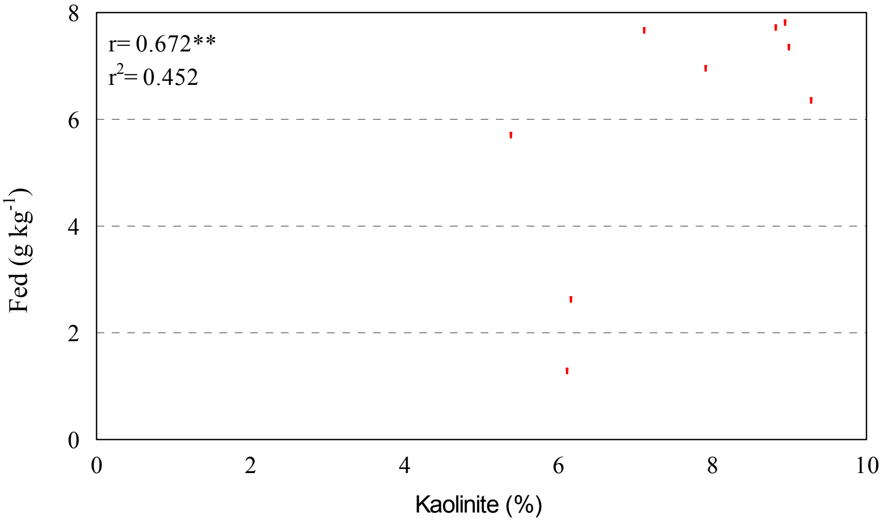
Figure 6.8: Relationships between Vermiculite and Feo and Kaolinite and Alo Contents for Bulk Samples (<2 mm) from the Königstein Profile

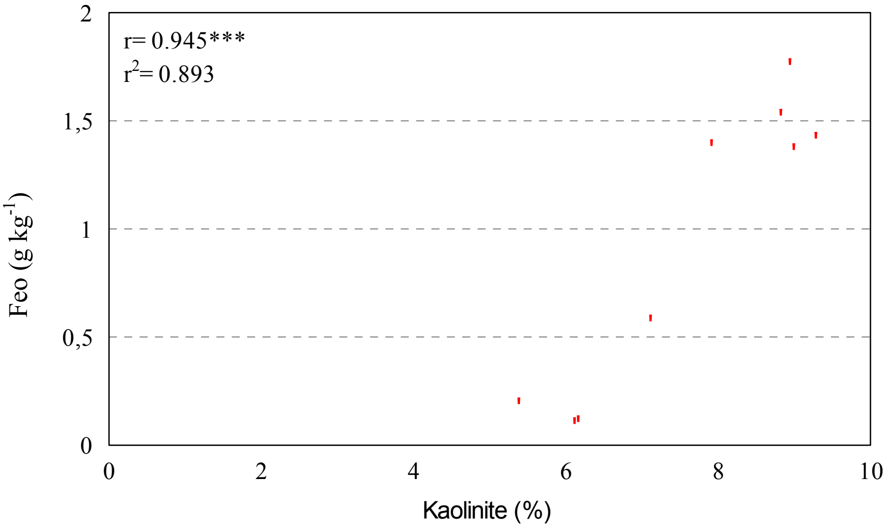




In the Geinsheim profile, Alo and Feo display significant relationships with a variety of clay minerals. Fed and Alo exhibit positive relationships with kaolinite (i.e. $r = 0.672$ ($p < 0.05$) and $r = 0.644$ ($p < 0.10$), respectively). Feo correlates positively with mixed layer illite/smectite (i.e. $r = 0.649$ ($p < 0.10$)), as well as with kaolinite (i.e. $r = 0.945$ ($p < 0.01$)). Figure 6.9 displays the scatter plots for kaolinite and Fed and Feo for the Geinsheim profile. The correlations between Fed and especially Feo and kaolinite support evidence in the literature that Fe has a high tendency to form coatings on the surfaces of this mineral, leading to aggregates and concretions that may serve to protect organic material (Tan 1998). This mechanism is perhaps a very important one in the preservation of organic matter in the Geinsheim profile.

Figure 6.9: Relationships between Kaolinite and Fed and Feo for Bulk Samples (<2 mm) from the Geinsheim Profile





As oxides are not as strongly associated with organic materials in the two Münden profiles compared to the other soils, clay-oxide-organic complexes would appear to be less important in protecting organic matter at these sites. Feo and Alo display a significant correlation with OC in the subsoil of the Münden 1 profile. However, only Feo correlates positively with vermiculite (i.e. $r = 0.840$ ($p < 0.05$)). This suggests the possible existence of vermiculite-Fe-organic complexes in this soil. As already mentioned though, this result is not reliable given the low sample number for the subsoil. For Münden 2, only Alo correlates significantly with the OC and N contents of bulk subsoil samples. Alo, in turn, correlates positively with chlorite (i.e. $r = 0.754$ ($p < 0.05$)). This mineral does not exhibit a significant positive relationship with OC, however. It is, therefore, unlikely to form complexes with this oxide and organic matter. With respect to the Frankfurter Stadtwald profile, there are virtually no correlations between clay minerals and oxides which suggests that a similar mechanism may play a role in protecting organic matter in this soil.

Overall, the evidence suggests that oxides, notably amorphous Al and Fe oxides, are very important in stabilizing organic matter in the soils under investigation. Clay-oxide-organic complexes are also suspected to help stabilize organic material to varying degrees. Particularly with respect to the Königstein and Geinsheim profiles, this mechanism may be rather significant in the preservation of organic material. In terms of the latter profile, kaolinite is most likely to interact with oxides, especially amorphous Fe, to form aggregates which protect organic matter. Clay-oxide-organic complexes would appear to be insignificant or non-existent in the Münden 2 and Frankfurter Stadtwald profiles. Oxides are more likely to singularly bind with organic material in these soils.

7. Conclusions

In sum, the results of this study provide evidence that the clay content and clay mineral composition of the soils under investigation in this study plays a limited role in the stabilization of organic matter. This is supported by a number of observations:

- Clay content correlates positively with the OC concentrations of bulk samples for only two of the profiles, Königstein and Geinsheim. For the Königstein soil profile, however, it is not clear whether a relationship actually exists between these two variables, as clay content decreases with depth as do OC contents. The former may not necessarily be a causal agent of the latter.
- Geinsheim and Frankfurter Stadtwald do not exhibit greater concentrations of OC and N in bulk soils, as would be predicted given their considerably greater clay contents. This is despite the fact that large amounts of smectite minerals are present in these two profiles, which are believed to have a greater capacity to retain organic matter given their larger surface area and potential capacity to intercalate organic compounds.
- There are only a limited number of clay minerals which exhibit significant positive correlations with OC and N contents in the profiles of concern. While smectite did not display a positive relationship with organic matter in the Geinsheim profile, kaolinite, for instance, was observed to correlate significantly with both the OC and N contents of samples.
- Exchangeable cations, which appear to have a high affinity for organic matter in the soil profiles, are positively related to only a few clay minerals, an indicator that clay minerals may be indirectly involved in the stabilization of organic material.

Additionally, it becomes evident that the relationship between SSA and OC concentrations, as originally proposed by Mayer (1994a), is not a ubiquitous one that is applicable to all soils. Most of the OC loadings of the silt and clay size fractions isolated from bulk samples do not fall into the predicted ME range of 0.6 to 1.5 mg OC m^{-2}. For the profiles Münden 1 and 2 and Königstein, the A horizons exhibited loadings greater than a monolayer coverage of organic material on mineral surfaces. Values for the B and C horizons for all profiles generally fell below the ME level. Results presented in the literature regarding the application of the “monolayer equivalent” concept to soils, however, is also contradictory. Similar to the results here, both Mayer (1994b) and Mayer and Xing (1999) demonstrated that a great number soils had OC loadings either above or below the ME. These findings suggest that the application of this concept to soils is perhaps inappropriate.

The fact that most of the samples had OC loadings that did not correspond to Mayer's (1994a) ME level does not mean, however, that adsorptive processes and the SSA of soils are not unimportant in the preservation of organic matter. Organic matter is not expected to simply be evenly distributed on the surfaces of minerals, but is more likely to be localized as patches and present as multilayer coatings both on and between minerals. Even Mayer, himself (see Mayer (1999) and Mayer and Xing (2001)), now warns against the usage of the term "monolayer equivalent" as it can be misleading. With respect to the profiles here, SSA exhibited a significant positive relationship with the OC content of two of the five profiles, Königstein and Geinsheim. For the former soil profile, this relationship only emerges when the topsoil is excluded from analysis. The large organic inputs to the Königstein profile, combined with a low pH, likely obscure any relationships between SSA and organic matter for this soil. The fact that the greatest OC concentrations are generally associated with the smallest particle size fractions but that strong significant relationships between clay content, clay mineral composition, SSA and OC concentrations are absent for most profiles suggests that adsorptive processes may not be as important as that propagated in the literature. Other factors must be present that are equally or even more important in the stabilization of organic matter in these soils such as the microporosity of soil, which tends to be greatly enhanced with the presence of both clay minerals and oxides.

This study provides evidence that oxides play an important role in the stabilization of organic material in the soils under investigation, as evidenced by the number of very strong, highly significant correlations between Feo, Alo and OC and N concentrations. The greater affinity of organic matter for oxides compared to clay minerals has also been demonstrated by other studies (e.g. Jones and Edwards 1998). A closer association between negatively charged humic substances and oxides would, of course, be predicted given the fact that oxides would be expected to carry a positive charge in the soil profiles due to their low pH. The permanent negative charge of clay minerals, in contrast, would likely repel most organic compounds. As discussed though, clay minerals may not be completely insignificant in stabilizing organic materials. Cations may serve as bridges between organic matter and clay minerals. The statistical results suggest, however, that this mechanism plays a limited role in the stabilisation of organic material in the soils investigated. Clay minerals may also be coated by oxides which, in turn, bind organic material, forming complexes which result in the aggregation and cementation of particles. This is likely to be an important mechanism in the preservation of organic matter in the Geinsheim and Königstein profiles. In the Geinsheim soil, kaolinite may, however, bind organic material directly. Similar to the oxides, kaolinite has broken edges with exposed hydroxyl groups which are amphoteric (Theng 1974; Tan 1998). This mineral may not carry a positive charge under the neutral pH conditions of the Geinsheim profile though and, thus, may not strongly sorb negatively charged humic substances.

In light of the results of this study, the presence of amorphous Fe and Al oxides appears to be an important factor in the stabilization of organic materials in the soils under investigation. The greater OC concentrations observed for the smallest particle size fractions compared to the other particle size separates for all profiles are likely due in large part to the fact that oxides tend to fall in these size fractions. In general, clay minerals are likely to play a secondary role in the preservation of organic matter. The significance of clay minerals should not be underestimated however. They particularly appear to be important in the Königstein and Geinsheim profiles. The lack of a significant relationship between clay content and SSA and organic matter for the other profiles suggests, however, that mechanisms apart from the adsorption of organic materials on clay surfaces plays a decisive role in different soils. Given the results here and that presented in the literature, the following models of organic matter stabilization are proposed:

- Strong adsorptive processes are involved in the stabilization of organic material by oxides for most soil profiles, particularly where soil conditions are acidic,
- Clay minerals help stabilize organic material by forming complexes with oxides which provide the basis of aggregates and concretions, as well as increase the microporosity of a soil.

Of course, the above does not suggest that the adsorption of organic matter on clay mineral surfaces or that the geometry of oxides, which helps to enhance the number of small pores in a soil within which organic particles may be protected, do not play a role in the stabilization of organic matter. Adsorptive processes are suggested to be more important in terms of oxides though, while indirect or physical mechanisms are likely to play a greater role in terms of clay minerals.

Regardless of the mechanisms involved, however, the question remains as to whether organic matter can be preserved over a longer time scale in soils and, therefore, act as a sink for atmospheric carbon. Progressive decreases in the OC content of both bulk soils and clay size fractions for the soil profiles with depth suggest that organic material is not permanently stabilized but is degraded over time. Organic material would appear to be preserved to some extent in the Geinsheim profile as evidenced by more stable OC carbon contents. It is unclear, however, whether this is due to some protective mechanism or whether this is simply a reflection of the self-mulching activity of the smectites in this soil, which causes organic matter to be transported down the soil profile.

8. Outlook

The primary purpose of this study was to investigate possible mechanisms, notably sorptive processes and the role of clay minerals, in the stabilization of a variety of German soils exhibiting different mineralogical characteristics. The goal of this was to contribute to current gaps in the knowledge base regarding the dynamics of soil organic matter within the context of global change and the role of soils in the alleviation of elevated atmospheric CO_2 levels. Of course, the question of whether soils can act as a long term sink for organic carbon from the atmosphere cannot be answered conclusively given the findings presented here based on five soil profiles. Together with results and hypotheses presented in the literature regarding both soils on a local level and our knowledge regarding global carbon dynamics, we can, however, postulate some tentative conclusions. These will be discussed below.

The role of soils in the global carbon cycle and their importance as a sink for atmospheric carbon has been a topic of interest and debate in attempts to identify solutions to slow global warming processes. This has in part been stimulated by Article 3.4 of the Kyoto Protocol, which suggests that "*sources and removals by sinks in the agricultural soils and the land-use change and forestry categories*" be considered in the future, opening up the way for countries to use soils to meet their emission reductions. Increases in atmospheric CO_2 levels since the 1800's appear to have lead to increases in primary productivity and corresponding greater amounts of carbon being stored in vegetation. The effects of increased CO_2 levels have been demonstrated in short-term chamber experiments which have shown that photosynthetic rates increase and foliar respiration decreases under conditions of elevated CO_2 (Norby et al. 1992; Luxmoore et al. 1993; Curtis et al. 1996). Observed increases in vegetation activity in the Northern hemisphere inferred from atmospheric CO_2 levels also support this (Keeling et al. 1996). The potential effects of enhanced levels of atmospheric CO_2 may also be intensified by N deposition (Curtis et al. 1996), the amounts of which have increased dramatically in many areas of the world due to fossil fuel emissions. Although the amount of carbon which may be stored in forests is potentially substantial due to such climatic effects, this is expected to decrease over time as forests age. Annual carbon sequestration in German forests, for instance, have been estimated to decrease from about 3 Tg C yr^{-1} in 1990 to 0.35 Tg C yr^{-1} by the year 2090 using the Frankfurt Biosphere Model (Häger et al. 1998).

Whether increases in carbon stored as biomass results in enhanced amounts of organic material being sequestered in soils is, however, unclear. Of course, soils can be managed to increase the amount of organic matter stored (for an overview see Batjes 1999). For instance, a reduced reliance on mechanical tillage methods and increased levels of crop residues left after harvest can serve to enhance the organic matter contents of agricultural soils. The conversion of agricultural land to grassland or forest can also result in a substantial accumulation of soil organic matter over time. For most soils, however, the amount of organic material which can be stored would likely be limited. If, for instance, the organic content of a soil is largely controlled by adsorptive processes, we can assume that the amount of mineral surface area available would be a limiting factor. Hassink (1997) compared the C and N contents of silt and clay fractions of a number of uncultivated soils in temperate and tropical regions and found that concentrations were the same, indicating that a maximum of C and N which can be associated with these fine fractions had been reached. Additionally, concentrations did not seem to be affected by clay mineral type.

Schlesinger (1990) estimated that global soils have a maximum carbon sequestration potential of 2.4 g C m^2 yr^{-1}, which amounts to about 0.4 Pg C yr^{-1} from the atmosphere. This is rather small compared to the size of the “missing sink”, which has been estimated to be as high as 1.8 Pg C yr^{-1} (Houghton et al. 1998). Additionally, most soils would appear unlikely to serve as a permanent sink for organic material. Although mechanisms such as the adsorption of organic material on oxides help stabilize organic material, these do not appear strong enough to result in a permanent preservation of OC. This is evidenced by the fact that OC concentrations progressively decrease with depth in the soils studied here.

Furthermore, soils may have less of a capacity to preserve carbon over time. Torn et al. (1997), for instance, suggest that many soils of the world will automatically become sources of CO_2 as they age. Specifically, they point out that about 25% of the world’s organic matter is stored in soils that have developed since the last major deglaciation. As the minerals become more mature, crystalline and less reactive over time, it is believed that they will lose their capacity to stabilize organic matter.

It could be argued, in fact, that many soils in the world will become major sources of CO_2 in the future. Wetlands, which are historic sinks for carbon, are already sources of CO_2 in many parts of the world (Eswaran et al. 1995). As they are drained for building and agricultural purposes, a major proportion of the C becomes lost in the form of CO_2. Further, soils which have served as carbon sinks in the past, especially in Northern areas, are likely to become sources for CO_2 as the climate continues to change and temperatures increase due to the effects of global warming (Kohlmaier 1989). Soils in some boreal areas of Canada, for instance, are already net sources of CO_2 due to increased thaw as a result of temperature changes and the resultant effects of mineralization rates (Goulden et al. 1998). Permafrost is expected to disappear in many areas in the future if global temperatures reach their predicted increase of about 2 °C by 2100 , which could result in large amounts of CO_2 being released to the atmosphere.

In light of the above, management attempts to increase the carbon storage capacity may help to alleviate climatic problems associated with elevated levels of atmospheric CO_2. This capacity may, however, be limited and only short-term and predicted increases in global temperatures may counteract efforts to increase carbon uptake by soils. Longer term solutions require that greenhouse gas emissions be reduced over time. This, of course, necessitates global participation and the development of creative solutions to help developing countries keep their respective predicted CO_2 emissions to a minimum.

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Appendix A: Soil Horizon Designations

WRB Soil Horizon Designations Used (from FAO, ISRIC and ISSS 1998)

O	horizon dominated by organic material
A	mineral horizon formed below an O horizon or at the surface of a soil, which is distinctly different from an E, B or C horizon
B	subsurface mineral horizon formed below an A, E or O horizon, where the original rock structure is no longer identifiable
C	subsurface horizon which lies below the solum, does not display the properties of an O, A, B or C horizon and which is minimally affected by pedogenic processes; includes sediments, unconsolidated bedrock and other geologic materials
E	mineral horizon which displays loss of silicate clay, iron and/or aluminium, leaving a dominance of sand and silt particles; the original rock structure is no longer identifiable

BK Soil Horizon Designations Used (from AG Boden 1994)

L	organic horizon dominated by undecomposed or partially decomposed plant material
O	organic horizon dominated by degraded plant material
Ah	A or upper mineral horizon formed below the organic layer at the surface of a soil, with as much as 30% organic material
Aeh	A or upper mineral horizon with as much as 30% organic material, which is weakly podzolized, with vertical variability in organic material
Ahe	A or upper mineral horizon which is partially or fully podzolized, with bleached spots, violet hues and horizontal variability in the distribution of organic material; Munsell colour value of 4 or more
Al	A or upper mineral horizon characterized by the downward movement of clay minerals; lighter in colour than the Ah and Bt horizons
fAxh	relict (i.e. f= fossilized) Ah horizon with high aggregate stability and a base saturation of >50%; displays signs of bioturbation
Bt	subsurface mineral horizon (i.e. B horizon), characterized by an illuvial accumulation of clay
Bv	subsurface mineral horizon (i.e. B horizon), where the original rock structure is no longer identifiable due to erosion, the presence of brown-coloured iron oxides and the formation of clay minerals
sBv	Bv horizon which is influenced by the presence of water
sBtv	subsurface Bt horizon affected by the presence of water with an illuvial accumulation of clay which is less than that observed between the Al and Bt horizons of the same soil
Cv	subsurface mineral horizon which lies below the solum with weathered geological material
ilCv	Cv horizon which is easy to dig (i.e. loose material) and has a high pebble/gravel content
ilsCv	Cv horizon which is easy to dig (i.e. loose material), has a high pebble/gravel content and is affected by the presence of water
Sd	subsoil mineral horizon which hinders the infiltration of water, causing water to stagnate in the above horizon; 50-70% of the horizon has rust- and bleached-spots
Sw	subsoil mineral horizon affected by stagnating water; >80% of the surface displays signs of oxidation and “bleaching” (i.e. lighter in colour)
Go	mineral horizon with hydromorphic properties caused by groundwater; >10% of the surface has rust spots or both rust and carbonate spots; either located in the zone of fluctuating groundwater levels or in the capillary fringe
Gco	Go horizon enriched in carbonates (min. 5% carbonate by weight)
Gcro	Gco horizon with partially reduced conditions; rust spots comprise 5-10% of the surface
Gr	mineral horizon with reduced conditions due to the presence of groundwater

Roman numerals assigned to the soil horizon designations are used to specify profile layers that have different parent materials.

Appendix B: Descriptive Soil Parameters of the Profiles Investigated

Profile 1: Münden 1

Table B.1: pH Values of Münden 1 Bulk Samples (<2 mm)

Depth (cm)	Horizon	pH- $CaCl_2$
0-5	Aeh	2.88
5-10	Ahe-Bv	3.03
10-20	Ah-Bv	3.50
20-30	Bv	3.84
30-60	sBv	3.84
60-80	IIBvCv	3.81
80-100	IIiICv	3.77

Table B.2: Dry Substance Content (%) of Münden 1 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Dry Substance (%)
0-5	Aeh	61.65
5-10	Ahe-Bv	84.07
10-20	Ah-Bv	84.34
20-30	Bv	88.89
30-60	sBv	86.58
60-80	IIBvCv	88.16
80-100+	IIiICv	88.56

Table B.3: Total Organic Matter Content (%) of Münden 1 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Total Organic Matter (%)
0-5	Aeh	28.09
5-10	Ahe-Bv	7.37
10-20	Ah-Bv	4.74
20-30	Bv	2.92
30-60	sBv	1.98
60-80	IIBvCv	2.53
80-100+	IIiICv	3.03

Table B.4 : Carbonate Content (%) of Münden 1 Bulk Samples (<2 mm)

Depth (cm)	Horizon	$CaCO_3$ (%)
0-5	Aeh	0.40
5-10	Ahe-Bv	0.34
10-20	Ah-Bv	0.18
20-30	Bv	0.20
30-60	sBv	0.37
60-80	IIBvCv	0.68
80-100+	IIiICv	0.33

Table B.5: Particle Size Distribution (%) of Münden 1 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Coarse Sand	Medium Sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
0-5	Aeh	1.03	3.10	8.75	28.15	28.70	9.68	20.25
5-10	Ahe-Bv	0.38	2.05	4.40	40.72	26.68	8.65	16.92
10-20	Ah-Bv	0.76	1.63	3.99	41.54	27.33	7.99	16.58
20-30	Bv	0.59	1.52	3.87	44.24	26.23	7.69	15.83
30-60	sBv	1.80	3.20	5.86	46.31	18.87	6.23	17.25
60-80	IIBvCv	3.50	7.06	17.63	27.15	14.33	7.43	22.32
80-100+	IIiICv	3.32	7.65	25.86	13.85	13.39	8.86	26.62

Profile 2: Münden 2

Table B.6: pH Values of Münden 2 Bulk Samples (<2 mm)

Depth(cm)	Horizon	pH- $CaCl_2$
0-5	Ah	3.10
5-10	Al	3.62
10-20	Al	3.67
20-50	Sw-Bt	3.74
50-70	Sd-Bt	3.72
70-90	sBtv	3.92
90-110	sBv	4.18
110-140	IIiIsCv	4.28
140-160+	IIiICv	4.36

Table B.7: Dry Substance Content (%) of Münden 2 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Dry Substance (%)
0-5	Ah	53.58
5-10	Al	71.98
10-20	Al	75.93
20-50	Sw-Bt	78.25
50-70	Sd-Bt	78.06
70-90	sBtv	79.93
90-110	sBv	79.90
110-140	IIiIsCv	79.84
140-160+	IIiICv	81.46

Table B.8: Total Organic Matter Content (%) of Münden 2 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Total Organic Matter (%)
0-5	Ah	19.85
5-10	Al	3.67
10-20	Al	3.35
20-50	Sw-Bt	2.22
50-70	Sd-Bt	2.19
70-90	sBtv	2.00
90-110	sBv	1.85
110-140	IIiIsCv	1.76
140-160+	IIiICv	1.76

Table B.9: Carbonate Content (%) of Münden 2 Bulk Samples (<2 mm)

Depth (cm)	Horizon	$CaCO_3$ (%)
0-5	Ah	0.78
5-10	Al	0.39
10-20	Al	0.54
20-50	Sw-Bt	0.51
50-70	Sd-Bt	0.32
70-90	sBtv	0.36
90-110	sBv	0.21
110-140	IIiIsCv	0.45
140-160+	IIiICv	0.61

Table B.10: Particle Size Distribution (%) of Münden 2 Bulk Samples (<2 mm)

Depth (cm)	Horizon	Coarse Sand	Medium Sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
0-5	Ah	0.87	0.83	3.04	45.64	23.89	7.76	17.98
5-10	Al	0.50	1.13	2.98	53.24	21.99	5.40	14.65
10-20	Al	0.22	0.97	2.45	48.70	25.42	5.13	16.28
20-50	Sw-Bt	0.48	0.80	1.62	49.74	21.55	5.18	20.63
50-70	Sd-Bt	0.45	0.65	1.57	45.52	22.34	5.11	24.11
70-90	sBtv	0.42	0.81	1.78	44.60	21.64	5.06	24.51
90-110	sBv	0.37	0.75	1.75	52.65	18.55	4.54	21.39
110-140	IIiIsCv	0.29	0.88	2.12	51.14	19.86	4.53	20.82
140-160+	IIiICv	0.61	1.45	3.89	48.91	19.35	4.62	21.02

Profile 3: Königstein

Table B.11: pH Values of Königstein Bulk Samples (<2 mm)

Depth (cm)	Horizon	pH- $CaCl_2$
0-5	Aeh	3.20
5-10	Ah-Bv	3.28
10-25	Bv	3.84
25-45	IIBv	3.90
45-65	IIBv	3.87
65-85	IIIBvCv	3.84
85+	IViCv	3.84

Table B.12: Dry Substance Content (%) of Königstein Bulk Samples (<2 mm)

Depth (cm)	Horizon	Dry Substance (%)
0-5	Aeh	59.28
5-10	Ah-Bv	73.84
10-25	Bv	79.95
25-45	IIBv	86.86
45-65	IIBv	88.23
65-85	IIIBvCv	86.99
85+	IViCv	91.09

Table B.13: Total Organic Matter Content (%) of Königstein Bulk Samples (<2 mm)

Depth (cm)	Horizon	Total Organic Matter (%)
0-5	Aeh	29.17
5-10	Ah-Bv	15.23
10-25	Bv	5.89
25-45	IIBv	3.78
45-65	IIBv	3.58
65-85	IIIBvCv	3.13
85+	IViCv	2.12

Table B.14: Carbonate Content (%) of Königstein Bulk Samples (<2 mm)

Depth (cm)	Horizon	$CaCO_3$ (%)
0-5	Aeh	0.27
5-10	Ah-Bv	0.37
10-25	Bv	0.36
25-45	IIBv	0.27
45-65	IIBv	0.40
65-85	IIIBvCv	0.33
85+	IViCv	0.30

Table B.15: Particle Size Distribution (%) of Königstein Bulk Samples (<2 mm)

Depth (cm)	Horizon	Coarse Sand	Medium Sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
0-5	Aeh	14.40	11.15	13.15	7.99	14.79	10.80	27.03
5-10	Ah-Bv	17.43	12.43	10.70	8.73	15.45	9.28	25.90
10-25	Bv	17.22	12.66	11.93	9.77	14.68	9.12	24.59
25-45	IIBv	16.38	15.45	14.20	10.85	13.66	9.84	18.85
45-65	IIBv	24.06	19.39	12.72	7.79	11.48	10.34	14.73
65-85	IIIBvCv	21.07	19.98	15.83	8.48	10.83	9.15	14.25
85+	IViCv	32.67	23.68	11.47	5.91	7.61	8.33	11.07

Profile 4: Geinsheim

Table B.16: pH Values of Geinsheim Bulk Samples (<2 mm)

Depth (cm)	Horizon	pH- $CaCl_2$
0-5	Ap	7.36
5-10	Ap	7.34
10-25	Ap	7.40
25-50	M	7.57
50-70	M	7.59
70-90	IIP	7.65
90-110	IIIfAxh-Go1	7.70
110-130	IIIfAxh-Gco2	7.79
130-150+	IVGcro4	7.69

Table B.17: Dry Substance Content (%) of Geinsheim Bulk Samples (<2 mm)

Depth (cm)	Horizon	Dry Substance (%)
0-5	Ap	78.13
5-10	Ap	78.04
10-25	Ap	78.48
25-50	M	80.58
50-70	M	77.65
70-90	IIP	79.18
90-110	IIIfAxh-Go1	82.91
110-130	IIIfAxh-Gco2	88.55
130-150+	IVGcro4	92.12

Table B.18: Total Organic Matter Content (%) of Geinsheim Bulk Samples (<2 mm)

Depth (cm)	Horizon	Total Organic Matter (%)
0-5	Ap	6.95
5-10	Ap	6.98
10-25	Ap	6.60
25-50	M	5.53
50-70	M	7.05
70-90	IIP	5.52
90-110	IIIfAxh-Go1	3.92
110-130	IIIfAxh-Gco2	2.78
130-150+	IVGcro4	1.24

Table B.19: Carbonate Content (%) of Geinsheim Bulk Samples (<2 mm)

Depth (cm)	Horizon	$CaCO_3$ (%)
0-5	Ap	3.82
5-10	Ap	3.71
10-25	Ap	4.72
25-50	M	3.89
50-70	M	2.44
70-90	IIP	2.58
90-110	IIIfAxh-Go1	6.51
110-130	IIIfAxh-Gco2	23.04
130-150+	IVGcro4	11.64

Table B.20: Particle Size Distribution (%) of Geinsheim Bulk Samples (<2 mm)

Depth (cm)	Horizon	Coarse Sand	Medium Sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
0-5	Ap	1.39	15.41	8.04	5.99	9.01	10.41	49.56
5-10	Ap	1.37	16.07	8.16	6.44	10.01	10.00	47.79
10-25	Ap	1.40	17.46	8.53	7.93	7.46	9.71	47.47
25-50	M	1.70	20.05	10.56	6.71	8.19	9.49	44.19
50-70	M	1.69	18.65	4.35	3.70	8.85	10.11	52.47
70-90	IIP	2.27	21.64	8.09	8.23	6.46	8.58	44.72
90-110	IIIfAxh-Go1	4.14	31.62	5.36	7.49	6.67	8.12	36.54
110-130	IIIfAxh-Gco2	10.61	47.70	7.18	6.01	5.21	5.47	17.25
130-150+	IVGcro4	16.89	63.54	7.31	2.35	2.42	1.88	5.58

Profile 5: Frankfurter Stadtwald

Table B.21: pH Values of Frankfurter Stadtwald Bulk Samples (<2 mm)

Depth (cm)	Horizon	pH- $CaCl_2$
0-5	Ah	3.65
5-10	Ah	3.37
10-15	AhGo	3.35
15-20	AhGo	3.45
20-25	AhGo	3.82
25-30	Go1	4.00
30-40	Go2	4.45
40-50	Gro1	4.92
50-60	Gro2	5.19
60-70	Gro2	5.41
70-80	Gro3	5.12
80-85	Gro3	5.34
85-90	IIGr	5.26
90-100	IIGr	5.17
100-110	IIGr	5.07

Table B.22: Dry Substance Content (%) of Frankfurter Stadtwald Bulk Samples (<2 mm)

Depth (cm)	Horizon	Dry Substance (%)
0-5	Ah	60.16
5-10	Ah	67.49
10-15	AhGo	70.43
15-20	AhGo	74.61
20-25	AhGo	78.27
25-30	Go1	77.75
30-40	Go2	78.17
40-50	Gro1	78.98
50-60	Gro2	77.96
60-70	Gro2	79.39
70-80	Gro3	82.39
80-85	Gro3	83.04
85-90	IIGr	87.02
90-100	IIGr	89.03
100-110	IIGr	86.23

Table B.23: Total Organic Matter Content (%) of Frankfurter Stadtwald Bulk Samples (<2 mm)

Depth (cm)	Horizon	Total Organic Matter (%)
0-5	Ah	18.82
5-10	Ah	15.64
10-15	AhGo	12.57
15-20	AhGo	7.16
20-25	AhGo	1.96
25-30	Go1	1.46
30-40	Go2	0.97
40-50	Gro1	0.83
50-60	Gro2	0.65
60-70	Gro2	0.55
70-80	Gro3	0.54
80-85	Gro3	0.62
85-90	IIGr	0.41
90-100	IIGr	0.44
100-110	IIGr	0.34

Table B.24: Carbonate Content (%) of Frankfurter Stadtwald Bulk Samples (<2 mm)

Depth (cm)	Horizon	$CaCO_3$ (%)
0-5	Ah	0.18
5-10	Ah	0.13
10-15	AhGo	0.03
15-20	AhGo	0.06
20-25	AhGo	0.13
25-30	Go1	0.03
30-40	Go2	0.10
40-50	Gro1	0
50-60	Gro2	0.03
60-70	Gro2	0.05
70-80	Gro3	0
80-85	Gro3	0.03
85-90	IIGr	0
90-100	IIGr	0.03
100-110	IIGr	0

Table B.25: Particle Size Distribution (%) of Frankfurter Stadtwald Bulk Samples (<2 mm)

Depth (cm)	Horizon	Coarse Sand	Medium Sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
0-5	Ah	2.03	3.60	5.09	15.46	17.63	8.81	47.39
5-10	Ah	1.54	3.75	4.59	16.96	18.02	9.08	46.06
10-15	AhGo	1.43	3.37	3.84	16.40	17.92	8.71	48.33
15-20	AhGo	2.20	3.91	3.82	16.79	17.26	9.55	46.47
20-25	AhGo	2.42	4.22	4.37	17.84	14.44	8.60	48.11
25-30	Go1	1.58	3.38	4.16	17.22	14.67	8.72	50.28
30-40	Go2	1.13	2.94	5.22	14.32	16.13	9.76	50.50
40-50	Gro1	0.42	2.78	6.19	16.87	14.89	11.46	47.39
50-60	Gro2	0.38	2.41	4.93	16.85	15.79	10.49	49.16
60-70	Gro2	0.12	1.79	4.27	15.98	15.78	12.64	49.42
70-80	Gro3	0.12	1.16	1.84	15.14	17.53	13.38	50.82
80-85	Gro3	1.32	9.33	6.51	20.24	17.02	9.97	35.60
85-90	IIGr	17.83	68.65	6.91	1.63	0.71	0.20	4.07
90-100	IIGr	15.59	17.63	8.25	0.00	0.93	0.62	2.99
100-110	IIGr	14.78	79.48	2.78	0.82	0.20	0.10	1.83

Appendix C: Organic Carbon (OC) and Nitrogen (N) Contents and C:N Ratios of the Bulk and Particle Size Fractions

Profile 1: Münden 1

Table C.1: OC and N Contents and C:N Ratios of Bulk Soil Samples (<2 mm) from the Münden 1 Profile

Depth (cm)	Horizon	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	74.11	2.87	26
5-10	Ahe-Bv	39.40	1.36	29
10-20	Ah-Bv	19.74	0.77	27
20-30	Bv	11.56	0.61	19
30-60	sBv	5.03	0.42	12
60-80	IIBvCv	4.47	0.29	16
80-100+	IIiICv	2.14	ND	NA

Note: ND= Non-Detectable
NA= Non-Applicable

Table C.2: OC and N Contents and C:N Ratios of the Sand Size Fractions (2000-63µm) from the Münden 1 Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	2000-630	7.48	0.35	21
		630-200	7.53	0.26	29
		200-63	2.58	0.09	29
5-10	Ahe-Bv	2000-630	7.10	0.49	14
		630-200	4.85	0.41	12
		200-63	1.72	0.15	11
10-20	Ah-Bv	2000-630	4.51	0.37	12
		630-200	3.44	0.31	11
		200-63	3.07	0.29	11
20-30	Bv	2000-630	1.96	0.15	13
		630-200	2.64	0.16	17
		200-63	3.41	0.23	15
30-60	sBv	2000-630	1.85	0.13	14
		630-200	1.43	0.08	19
		200-63	2.01	0.16	13
60-80	IIBvCv	2000-630	1.04	0.24	4
		630-200	1.47	0.14	11
		200-63	0.76	0.08	10
80-100+	IIiICv	2000-630	1.05	0.12	9
		630-200	1.20	0.30	4
		200-63	1.07	0.13	8

Table C.3: OC and N Contents and C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Münden 1 Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	<63	107.78	4.21	26
		<20	138.90	5.44	26
		<6.3	166.22	6.33	26
		<2	164.63	7.43	22
		<1	151.04	7.95	19
5-10	Ahe-Bv	<63	36.15	1.37	26
		<20	63.86	2.22	29
		<6.3	114.68	3.62	32
		<2	114.03	4.17	27
		<1	101.11	4.29	24
10-20	Ah-Bv	<63	24.50	1.06	23
		<20	41.64	1.63	26
		<6.3	68.02	2.50	27
		<2	69.52	2.81	25
		<1	60.37	2.76	22
20-30	Bv	<63	10.88	0.85	13
		<20	17.34	1.30	13
		<6.3	31.79	1.84	17
		<2	35.51	1.90	19
		<1	33.42	1.77	19
30-60	sBv	<63	5.80	0.61	10
		<20	6.64	0.76	9
		<6.3	7.00	0.68	10
		<2	13.31	1.00	13
		<1	14.00	0.96	15
60-80	IIBvCv	<63	4.12	0.80	5
		<20	9.08	1.07	8
		<6.3	4.90	0.20	25
		<2	6.66	0.92	7
		<1	7.97	1.02	8
80-100+	IIiICv	<63	2.22	0.40	6
		<20	3.29	0.69	5
		<6.3	3.10	0.10	31
		<2	6.76	0.87	8
		<1	9.74	1.23	8

Profile 2 :Münden 2

Table C.4: OC and N Contents and C:N Ratios of Bulk Soil Samples (<2 mm) from the Münden 2 Profile

Depth (cm)	Horizon	OC Content ($g\ kg^{-1}$)	N Content ($g\ kg^{-1}$)	C:N Ratio
0-5	Ah	64.47	3.48	18.55
5-10	Al	5.21	0.43	12.25
10-20	Al	9.79	0.48	20.40
20-50	Sw-Al	5.11	0.50	10.22
50-70	Sd-Bt	6.59	0.60	10.98
70-90	sBtv	5.88	0.41	14.34
90-110	sBv	3.81	0.50	7.62
110-140	IIiIsCv	1.98	0.39	5.08
140-160+	IIiICv	4.18	0.35	11.94

Table C.5: OC and N Contents and C:N Ratios of the Sand Size Fractions (2000-63) from the Münden 2 Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content ($g\ kg^{-1}$)	N Content ($g\ kg^{-1}$)	C:N Ratio
0-5	Ah	2000-630	11.53	0.66	18
		630-200	10.37	0.68	15
		200-63	2.91	0.37	8
5-10	Al	2000-630	10.99	0.48	23
		630-200	14.39	0.53	27
		200-63	4.35	0.20	22
10-20	Al	2000-630	8.14	0.40	21
		630-200	12.14	0.64	19
		200-63	2.45	0.17	14
20-50	Sw-Al	2000-630	5.05	0.46	11
		630-200	4.90	0.32	15
		200-63	12.29	0.85	14
50-70	Sd-Bt	2000-630	3.38	0.23	15
		630-200	7.16	0.47	15
		200-63	6.23	0.54	12
70-90	sBtv	2000-630	2.82	0.37	8
		630-200	2.35	0.34	7
		200-63	7.48	0.80	9
90-110	sBv	2000-630	1.18	0.24	5
		630-200	2.27	0.21	11
		200-63	2.85	0.20	14
110-140	IIiIsCv	2000-630	0.56	0.38	1
		630-200	1.50	0.12	13
		200-63	2.32	ND	NA
140-160+	IIiICv	2000-630	1.16	0.32	4
		630-200	1.07	0.35	3
		200-63	1.82	0.23	8

Note: ND= Non-Detectable
NA= Non-Applicable

Table C.6: OC and N Contents and C:N Ratios of the Silt and Clay Size Fractions (<63 μm) from the Münden 2 Profile

Depth (cm)	Horizon	Fraction (μm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ah	<63	78.53	4.38	18
		<20	131.79	7.00	19
		<6.3	170.85	10.42	16
		<2	171.88	12.14	14
		<1	200.79	14.90	13
5-10	Al	<63	14.83	0.78	19
		<20	28.69	2.50	11
		<6.3	53.19	3.25	16
		<2	57.69	3.66	16
		<1	50.86	3.50	15
10-20	Al	<63	11.27	0.91	12
		<20	19.15	1.51	13
		<6.3	32.21	2.30	14
		<2	35.38	2.77	13
		<1	35.04	3.35	10
20-50	Sw-Al	<63	6.75	0.49	14
		<20	8.46	0.69	12
		<6.3	13.88	2.28	6
		<2	19.46	2.05	9
		<1	26.14	3.06	9
50-70	Sd-Bt	<63	6.22	0.65	10
		<20	14.08	1.04	14
		<6.3	23.25	1.54	15
		<2	26.59	2.11	13
		<1	29.00	2.71	11
70-90	sBtv	<63	2.35	0.29	8
		<20	5.61	1.01	6
		<6.3	12.08	0.87	14
		<2	8.33	1.58	5
		<1	8.03	1.51	5
90-110	sBv	<63	3.03	0.56	5
		<20	3.71	0.49	8
		<6.3	6.32	1.11	6
		<2	6.88	1.12	6
		<1	6.00	1.04	6
110-140	IIiIsCv	<63	3.01	1.65	2
		<20	4.20	0.99	4
		<6.3	14.14	1.05	13
		<2	9.94	1.94	5
		<1	15.22	1.07	14
140-160+	IIiICv	<63	2.45	0.53	5
		<20	3.08	0.65	5
		<6.3	4.97	0.80	6
		<2	4.16	0.73	6
		<1	5.36	0.97	6

Profile 3: Königstein

Table C.7: OC and N Contents and C:N Ratios of Bulk Soil Samples (<2 mm) from the Königstein Profile

Depth (cm)	Horizon	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	62.43	3.87	16
5-10	Ah-Bv	32.04	2.21	15
10-25	Bv	20.08	1.46	14
25-45	IIBv	6.39	0.71	9
45-65	IIBv	3.64	0.69	5
65-85	IIIBvCv	3.18	0.33	9
85-100+	IViCv	2.29	0.79	3

Table C.8: OC and N Contents and C:N Ratios of the Sand Size Fractions (2000-63 μm) from the Königstein Profile

Depth (cm)	Horizon	Fraction (μm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	2000-630	3.93	0.24	16
		630-200	3.55	0.17	21
		200-63	1.71	0.09	19
5-10	Ah-Bv	2000-630	2.92	0.18	16
		630-200	2.75	0.07	39
		200-63	2.74	0.11	25
10-25	Bv	2000-630	1.93	0.12	16
		630-200	2.66	0.08	33
		200-63	2.56	0.12	21
25-45	IIBv	2000-630	1.30	0.06	22
		630-200	1.43	0.17	8
		200-63	1.81	0.13	14
45-65	IIBv	2000-630	2.03	0.16	13
		630-200	0.98	0.38	3
		200-63	2.18	0.23	9
65-85	IIIBvCv	2000-630	1.27	0.54	2
		630-200	1.23	0.50	2
		200-63	1.50	0.55	3
85-100+	IViCv	2000-630	2.94	0.81	4
		630-200	1.62	0.61	4
		200-63	1.20	0.79	2

Table C.9: OC and N Contents and C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Aeh	<63	110.44	7.04	16
		<20	142.25	7.37	19
		<6.3	129.20	7.31	18
		<2	116.89	7.74	15
		<1	118.92	8.67	14
5-10	Ah-Bv	<63	43.28	3.90	11
		<20	48.55	3.94	12
		<6.3	69.93	4.66	15
		<2	47.79	5.16	9
		<1	55.63	5.84	10
10-25	Bv	<63	29.75	2.23	13
		<20	16.65	2.41	7
		<6.3	36.78	3.22	11
		<2	35.98	3.53	10
		<1	39.80	4.25	9
25-45	IIBv	<63	8.32	1.20	7
		<20	10.48	1.24	8
		<6.3	11.25	1.96	6
		<2	13.43	2.24	6
		<1	15.28	2.69	5
45-65	IIBv	<63	4.08	0.87	5
		<20	4.52	0.51	9
		<6.3	5.38	1.19	5
		<2	7.81	1.64	5
		<1	9.01	2.27	4
65-85	IIIBvCv	<63	4.54	0.94	5
		<20	4.46	0.84	5
		<6.3	6.93	0.66	11
		<2	11.64	0.79	15
		<1	17.34	4.27	4
85-100+	IViCv	<63	3.02	0.32	9
		<20	3.48	0.90	4
		<6.3	3.75	1.05	4
		<2	4.92	1.10	4
		<1	7.76	1.44	5

Profile 4: Geinsheim

Table C.10: OC and N Contents and C:N Ratios of Bulk Soil Samples (<2 mm) from the Geinsheim Profile

Depth (cm)	Horizon	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ap	20.84	2.19	10
5-10	Ap	16.77	2.07	8
10-25	Ap	15.17	1.90	8
25-50	M	12.97	0.82	16
50-70	M	15.49	1.48	10
70-90	IIP	8.15	0.46	18
90-110	IIIfAxh-Go1	3.85	0.76	5
110-130	IIIfAxh-Gco2	4.51	0.52	9
130-150+	IVGcro4	2.61	0.26	10

Table C.11: OC and N Contents and C:N Ratios of the Sand Size Fractions (2000-63 µm) from the Geinsheim Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ap	2000-630	24.11	0.90	27
		630-200	8.68	0.84	10
		200-63	5.65	0.73	8
5-10	Ap	2000-630	6.69	0.62	11
		630-200	1.32	0.62	2
		200-63	5.39	0.74	7
10-25	Ap	2000-630	5.07	0.68	7
		630-200	3.28	1.02	3
		200-63	0.97	0.79	1
25-50	M	2000-630	6.89	0.07	98
		630-200	0.33	ND	NA
		200-63	1.42	ND	NA
50-70	M	2000-630	1.52	0.02	76
		630-200	0.75	ND	NA
		200-63	4.01	0.05	80
70-90	IIP	2000-630	6.60	0.34	19
		630-200	2.98	0.05	60
		200-63	3.46	0.04	87
90-110	IIIfAxh-Go1	2000-630	3.65	0.36	10
		630-200	0.38	0.02	19
		200-63	2.25	0.14	16
110-130	IIIfAxh-Go2	2000-630	1.09	0.08	14
		630-200	1.84	0.07	26
		200-63	3.56	0.15	24
130-150+	IVGro4	2000-630	1.11	0.06	19
		630-200	0.59	0.05	12
		200-63	1.43	0.14	10

Note: ND= Non-Detectable
NA= Non-Applicable

Table C.12: OC and N Contents and C:N Ratios of the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ap	<63	15.90	1.89	8
		<20	17.62	2.10	8
		<6.3	18.24	2.41	8
		<2	22.45	3.01	7
		<1	26.40	2.29	12
5-10	Ap	<63	12.97	1.67	8
		<20	15.63	2.01	8
		<6.3	16.06	2.59	6
		<2	23.29	2.67	9
		<1	21.17	3.48	6
10-25	Ap	<63	13.67	2.36	6
		<20	29.39	2.62	11
		<6.3	15.77	3.19	5
		<2	21.51	3.27	7
		<1	20.30	4.08	5
25-50	M	<63	11.36	2.23	5
		<20	13.46	2.37	6
		<6.3	15.82	2.69	6
		<2	20.66	2.63	8
		<1	19.84	2.59	8
50-70	M	<63	14.62	1.38	11
		<20	14.46	1.46	10
		<6.3	15.81	1.15	14
		<2	24.65	1.73	14
		<1	24.44	1.60	15
70-90	IIP	<63	8.51	0.20	43
		<20	16.22	1.25	13
		<6.3	18.76	1.37	14
		<2	16.09	1.16	14
		<1	13.93	0.85	16
90-110	IIIfAxh-Go1	<63	15.46	1.31	12
		<20	14.95	1.22	12
		<6.3	10.02	1.48	7
		<2	14.09	1.30	11
		<1	14.49	1.15	13
110-130	IIIfAxh-Go2	<63	9.79	1.16	8
		<20	11.61	2.91	4
		<6.3	11.23	1.06	11
		<2	12.88	1.13	11
		<1	10.66	1.55	7
130-150+	IVGro4	<63	6.07	0.80	8
		<20	10.51	1.33	8
		<6.3	15.08	1.23	12
		<2	12.89	1.14	11
		<1	12.40	1.54	8

Profile 5: Frankfurter Stadtwald

Table C.13: OC and N Contents and C:N Ratios of Bulk Soil Samples (<2 mm) from the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ah	137.00	9.79	14
5-10	Ah	118.20	7.56	16
10-15	AhGo	82.48	5.46	15
15-20	AhGo	51.91	3.72	14
20-25	AhGo	15.89	1.12	14
25-30	Go1	12.86	1.18	11
30-40	Go2	8.20	0.64	13
40-50	Gro1	3.91	0.33	12
50-60	Gro2	4.21	0.19	22
60-70	Gro2	3.88	ND	NA
70-80	Gro3	3.03	0.21	14
80-85	Gro3	3.15	0.12	26
85-90	IIGr	2.61	0.50	5
90-100	IIGr	3.25	0.07	46
100-110	IIGr	2.63	0.09	29

Note: ND= Non-Detectable
NA= Non-Applicable

Table C.14: OC and N Contents and C:N Ratios of the Silt and Clay Fractions (<63 µm) from the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
0-5	Ah	<63	110.40	10.79	10
		<20	104.40	11.73	9
		<6.3	77.09	15.83	5
		<2	74.79	20.82	4
5-10	Ah	<63	105.70	4.72	22
		<20	106.60	9.26	12
		<6.3	109.90	13.11	8
		<2	130.40	18.92	7
10-15	AhGo	<63	47.13	4.30	11
		<20	49.67	4.72	11
		<6.3	55.41	5.71	10
		<2	55.47	6.20	9
15-20	AhGo	<63	32.28	3.28	10
		<20	36.90	3.74	10
		<6.3	39.54	4.32	9
		<2	40.09	4.48	9
20-25	AhGo	<63	12.58	1.77	7
		<20	14.39	2.01	7
		<6.3	16.31	2.45	7
		<2	16.97	2.76	6
25-30	Go1	<63	10.32	1.34	8
		<20	12.28	1.21	10
		<6.3	13.19	2.03	7
		<2	11.86	1.95	6
		<2	9.84	2.14	5

Table C.14 (continued): OC and N Contents and C:N Ratios of the Silt and Clay Fractions (<63 µm) from the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	Fraction (µm)	OC Content (g kg^{-1})	N Content (g kg^{-1})	C:N Ratio
30-40	Go2	<63	8.45	1.62	5
		<20	8.75	1.55	6
		<6.3	9.61	1.81	5
40-50	Gro1	<63	5.78	0.99	6
		<20	6.64	1.05	6
		<6.3	7.22	1.35	5
		<2	7.90	1.29	6
50-60	Gro2	<63	3.02	0.43	7
		<20	3.49	0.52	7
		<6.3	4.11	0.74	6
		<2	4.17	0.72	6
60-70	Gro2	<63	3.03	0.44	7
		<20	3.62	0.55	7
		<6.3	4.57	0.65	7
		<2	4.13	0.71	6
70-80	Gro3	<63	3.33	0.62	5
		<20	4.30	0.77	6
		<6.3	4.62	0.86	5
		<2	5.26	0.94	6
80-85	Gro3	<63	3.08	0.34	9
		<20	4.13	0.57	7
		<6.3	5.29	0.82	6
		<2	5.20	0.80	7
85-90	IIGr	<63	23.38	2.01	12
		<20	28.29	2.45	12
		<6.3	27.73	2.79	10
		<2	27.61	3.19	9
90-100	IIGr	<63	26.59	2.10	13
		<20	32.19	2.63	12
		<6.3	30.26	2.72	11
		<2	27.82	3.05	9
100-110	IIGr	<63	60.44	3.95	15
		<20	68.66	4.49	15
		<6.3	61.83	5.00	12
		<2	52.25	4.61	11

Appendix D: Potential Cation Exchange (CEC_{pot}) and Effective Cation Exchange (CEC_{eff}) Capacities and Exchangeable Cation Saturation

Profile 1: Münden 1

Table D.1: Potential Cation Exchange Capacity (CEC_{pot}) ($cmol_c\ kg^{-1}$) for Bulk Soil Samples (<2 mm) from the Münden 1 Profile

Depth (cm)	Horizon	CEC_{pot}	Na	K	Mg	Ca	H-Value
0-5	Aeh	61.70	0.08	0.17	0.33	1.68	59.44
5-10	Ahe-Bv	25.96	0.03	0.06	0.08	0.31	25.48
10-20	Ah-Bv	13.66	0.03	0.03	0.04	0.06	13.49
20-30	Bv	10.60	0.02	0.00	0.03	0.06	10.48
30-60	sBv	8.70	0.02	0.07	0.05	0.06	8.49
60-80	IIBvCv	9.18	0.01	0.10	0.06	0.06	8.99
80-100+	IIiICv	7.42	0.02	0.20	0.08	0.12	6.99

Table D.2: Effective Cation Exchange Capacity (CEC_{eff}) ($cmol_c\ kg^{-1}$) for Bulk Soil Samples (<2 mm) from the Münden 1 Profile

Depth (cm)	Horizon	CEC_{eff}	Fe	Mn	Al	H-Value
0-5	Aeh	29.55	0.32	0.04	9.98	16.95
5-10	Ahe-Bv	20.21	0.96	0.02	7.77	10.98
10-20	Ah-Bv	19.30	0.53	0.01	8.89	9.69
20-30	Bv	13.41	0.16	0.01	5.55	7.58
30-60	sBv	13.52	0.05	0.01	6.66	6.58
60-80	IIBvCv	13.90	0.05	0.01	6.66	6.99
80-100+	IIiICv	12.03	0.05	0.01	5.55	5.99

Table D.3: Exchangeable Cations (% Saturation) for Bulk Soil Samples (<2 mm) from the Münden 1 Profile

Depth (cm)	Horizon	Na	K	Mg	Ca	Fe	Mn	Al	H
0-5	Aeh	0.28	0.57	1.12	5.69	1.09	0.14	33.77	57.35
5-10	Ahe-Bv	0.13	0.28	0.41	1.54	4.77	0.09	38.45	54.32
10-20	Ah-Bv	0.17	0.15	0.21	0.32	2.75	0.08	46.08	50.23
20-30	Bv	0.16	0.00	0.23	0.46	1.20	0.11	41.34	56.49
30-60	sBv	0.16	0.54	0.38	0.46	0.40	0.11	49.25	48.70
60-80	IIBvCv	0.08	0.73	0.44	0.45	0.38	0.10	47.74	50.07
80-100+	IIiICv	0.14	1.65	0.69	1.04	0.45	0.12	46.15	49.78

Profile 2: Münden 2

Table D.4: Potential Cation Exchange Capacity (CEC_{pot}) ($cmol_c\ kg^{-1}$) for Bulk Soil Samples (<2 mm) from the Münden 2 Profile

Depth (cm)	Horizon	CEC_{pot}	Na	K	Mg	Ca	H-Value
0-5	Ah	41.06	0.05	0.32	0.40	1.31	38.98
5-10	Al	13.13	0.01	0.06	0.07	0.00	12.99
10-20	Al	10.58	0.01	0.05	0.03	0.00	10.49
20-50	Sw-Al	12.70	0.02	0.14	0.05	0.00	12.49
50-70	Sd-Bt	11.87	0.01	0.21	0.09	0.00	11.49
70-90	sBtv	12.34	0.02	0.20	0.88	1.25	10.00
90-110	sBv	13.88	0.04	0.18	2.06	2.62	7.50
110-140	IIiIsCv	11.38	0.04	0.18	1.60	3.06	6.50
140-160+	IIiICv	11.16	0.04	0.17	1.96	3.49	5.50

Table D.5: Effective Cation Exchange Capacity (CEC_{eff}) ($cmol_c$ kg^{-1}) for Bulk Soil Samples (<2 mm) from the Münden 2 Profile

Depth (cm)	Horizon	CEC_{eff}	Fe	Mn	Al	H-Value
0-5	Ah	28.12	0.64	0.13	11.09	14.16
5-10	Al	16.64	0.43	0.03	7.77	8.28
10-20	Al	12.44	0.16	0.05	5.55	6.58
20-50	Sw-Al	16.09	0.05	0.07	7.77	7.99
50-70	Sd-Bt	19.87	0.05	0.06	10.00	9.39
70-90	sBtv	15.71	0.05	0.07	6.66	6.59
90-110	sBv	22.50	0.05	0.05	3.33	3.79
110-140	IIiIsCv	9.94	0.00	0.05	2.22	2.80
140-160+	IIiICv	9.83	0.00	0.05	2.22	1.90

Table D.6: Exchangeable Cations (% Saturation) for Bulk Soil Samples (<2 mm) from the Münden 2 Profile

Depth (cm)	Horizon	Na	K	Mg	Ca	Fe	Mn	Al	H
0-5	Ah	0.19	1.13	1.43	4.66	2.29	0.48	39.46	50.37
5-10	Al	0.07	0.35	0.43	0.00	2.57	0.17	46.66	49.74
10-20	Al	0.09	0.39	0.25	0.00	1.29	0.44	44.61	52.94
20-50	Sw-Al	0.10	0.89	0.32	0.00	0.33	0.41	48.31	49.64
50-70	Sd-Bt	0.05	1.04	0.47	0.31	0.27	0.29	50.31	47.24
70-90	sBtv	0.10	1.28	5.59	7.94	0.34	0.42	42.40	41.93
90-110	sBv	0.36	1.45	17.01	21.57	0.44	0.42	27.47	31.28
110-140	IIiIsCv	0.38	1.83	16.10	30.73	0.00	0.48	22.35	28.13
140-160+	IIiICv	0.44	1.69	19.95	35.51	0.00	0.52	22.59	19.30

Profile 3: Königstein

Table D.7: Potential Cation Exchange Capacity (CEC_{pot}) ($cmol_c$ kg^{-1}) for Bulk Soil Samples (<2 mm) from the Königstein Profile

Depth (cm)	Horizon	CEC_{pot}	Na	K	Mg	Ca	H-Value
0-5	Aeh	69.98	0.05	0.21	0.72	6.54	62.45
5-10	Ah-Bv	43.02	0.02	0.09	0.28	2.18	40.46
10-25	Bv	19.86	0.01	0.01	0.04	.31	19.49
25-45	IIBv	10.19	0.01	0.02	0.05	.12	9.99
45-65	IIBv	9.63	0.01	0.03	0.03	.06	9.50
65-85	IIIBvCv	10.11	0.01	0.03	0.02	.06	9.99
85-100+	IViCv	7.61	0.00	0.04	0.02	.06	7.49

Table D.8: Effective Cation Exchange Capacity (CEC_{eff}) ($cmol_c$ kg^{-1}) for Bulk Soil Samples (<2 mm) from the Königstein Profile

Depth (cm)	Horizon	CEC_{eff}	Fe	Mn	Al	H-Value
0-5	Aeh	42.99	1.23	1.29	13.34	19.59
5-10	Ah-Bv	34.99	0.70	0.53	14.43	16.77
10-25	Bv	16.08	0.05	0.28	7.78	7.60
25-45	IIBv	9.67	0.00	0.23	4.45	4.80
45-65	IIBv	9.33	0.05	0.11	4.44	4.59
65-85	IIIBvCv	9.68	0.00	0.12	4.44	4.99
85-100+	IViCv	7.70	0.00	0.05	3.33	4.19

Table D.9: Exchangeable Cations (% Saturation) for Bulk Soil Samples (<2 mm) from the Königstein Profile

Depth (cm)	Horizon	Na	K	Mg	Ca	Fe	Mn	Al	H
0-5	Aeh	0.11	0.49	1.68	15.22	2.87	3.00	31.04	45.58
5-10	Ah-Bv	0.05	0.25	0.80	6.23	1.99	1.53	41.24	47.92
10-20	Bv	0.03	0.04	0.26	1.94	0.33	1.74	48.41	47.25
20-30	IIBv	0.06	0.20	0.53	1.29	0.00	2.33	45.98	49.61
30-60	IIBv	0.12	0.31	0.33	0.67	0.57	1.21	47.59	49.20
60-80	IIIBvCv	0.06	0.30	0.21	0.64	0.00	1.28	45.92	51.60
80-100+	IViCv	0.00	0.54	0.27	0.81	0.00	0.66	43.27	54.46

Profile 4: Geinsheim

Table D.10: Potential Cation Exchange Capacity (CEC_{pot}) ($cmol_c\ kg^{-1}$) for Bulk Soil Samples (<2 mm) from the Geinsheim Profile

Depth (cm)	Horizon	CEC_{pot}	Na	K	Mg	Ca	H-Value
0-5	Ap	34.66	0.18	0.85	2.48	31.16	0.00
5-10	Ap	36.49	0.24	0.94	2.58	32.73	0.00
10-25	Ap	30.88	0.26	0.42	2.17	28.04	0.00
25-50	M	40.24	0.26	0.18	3.04	36.76	0.00
50-70	M	47.10	0.23	0.14	4.03	42.70	0.00
70-90	IIP	43.31	0.20	0.13	4.34	38.65	0.00
90-110	IIIfAxh-Go1	35.78	0.14	0.09	4.08	31.47	0.00
110-130	IIIfAxh-Gco2	20.54	0.05	0.04	2.06	18.39	0.00
130-150+	IVGcro4	10.22	0.02	0.02	0.83	9.35	0.00

Table D.11: Exchangeable Cations (% Saturation) for Bulk Soil Samples (<2 mm) from the Geinsheim Profile

Depth (cm)	Horizon	Na	K	Mg	Ca	Fe	Mn	Al	H
0-5	Ap	0.52	2.44	7.15	89.90	0.00	0.00	0.00	0.00
5-10	Ap	0.66	2.58	7.07	89.69	0.00	0.00	0.00	0.00
10-25	Ap	0.83	1.38	7.02	90.78	0.00	0.00	0.00	0.00
25-50	M	0.65	0.44	7.56	91.35	0.00	0.00	0.00	0.00
50-70	M	0.50	0.31	8.55	90.65	0.00	0.00	0.00	0.00
70-90	IIP	0.45	0.30	10.01	89.24	0.00	0.00	0.00	0.00
90-110	IIIfAxh-Go1	0.39	0.25	11.39	87.96	0.00	0.00	0.00	0.00
110-130	IIIfAxh-Gco2	0.26	0.17	10.05	89.51	0.00	0.00	0.00	0.00
130-150+	IVGcro4	0.21	0.22	8.08	91.49	0.00	0.00	0.00	0.00

Appendix E: First Order Reflections and Mineral Composition of the Clay Size Fractions

Profile 1: Münden 1

Table E.1: First Order Reflections and Response to Glycolation for the Münden 1 Profile

Depth (cm)	Horizon	Smectite 16-17 Å (glycolated)			Chlorite + Vermiculite 14.5 Å			Mixed Layer 11-12 Å			Illite 10 Å			Kaolinite + Chlorite 7.1 Å		
		2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM
0-5	Aeh	ND	ND	ND	13.90	26	1.63	12.04	223	1.59	10.21	94	1.10	7.18	619	0.35
5-10	Ahe-Bv	ND	ND	ND	14.24	290	1.45	12.04	87	0.96	10.23	75	0.80	7.18	593	0.37
10-20	Ah-Bv	ND	ND	ND	14.01	196	1.09	11.84	86	1.04	10.26	90	0.85	7.18	493	0.37
20-30	Bv	NA	NA	NA	14.20	263	0.67	12.13	71	1.27	10.17	98	0.89	7.16	577	0.41
30-60	sBv	ND	ND	ND	14.08	169	1.26	11.60	118	0.96	10.10	372	0.95	7.16	821	0.42
60-80	IIBvCv	NA	NA	NA	14.05	71	0.49	11.02	134	1.33	10.02	1030	0.56	7.17	1614	0.35
80-100+	IIilCv	NA	NA	NA	ND	ND	ND	ND	ND	ND	10.01	1232	0.54	7.17	1689	0.35

Note: ND= Non-Detectable
NA= Non-Applicable

Profile 2: Münden 2

Table E.2: First Order Reflections and Response to Glycolation for the Münden 2 Profile

Depth (cm)	Horizon	Smectite 16-17 Å (glycolated)			Chlorite + Vermiculite 14.5 Å			Mixed Layer 11-12 Å			Illite 10 Å			Kaolinite + Chlorite 7.1 Å		
		2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM
0-5	Ah	-	-	-	13.12	54	1.73	11.17	65	0.99	10.24	124	0.68	7.17	175	0.36
5-10	Al	ND	ND	ND	14.27	261	0.94	11.82	79	1.32	10.12	64	0.65	7.17	250	0.45
10-20	Al	ND	ND	ND	14.30	283	0.90	11.98	94	1.26	10.24	81	0.86	7.19	277	0.47
20-50	Sw-Bt	NA	NA	NA	14.27	193	1.18	11.58	93	1.01	10.09	182	0.75	7.18	294	0.45
50-70	Sd-Bt	ND	ND	ND	14.15	200	1.45	11.43	75	1.18	10.12	162	0.82	7.16	170	0.48
70-90	sBtv	ND	ND	ND	14.12	189	1.69	11.16	92	1.04	9.99	208	0.62	7.14	324	0.39
90-110	sBv	ND	ND	ND	14.46	232	0.96	12.35	166	1.62	10.06	228	0.92	7.19	380	0.39
110-140	IIilsCv	NA	NA	NA	14.23	172	1.48	11.46	87	1.36	10.03	204	0.72	7.16	311	0.40
140-160+	IIilCv	NA	NA	NA	14.13	221	1.17	11.89	120	1.29	10.02	342	0.76	7.18	667	0.34

Note: ND= Non-Detectable
NA= Non-Applicable

Profile 3: Königstein

Table E.3: First Order Reflections and Response to Glycolation for the Königstein Profile

Depth (cm)	Horizon	Smectite 16-17 Å (glycolated)			Chlorite + Vermiculite 14.5 Å			Mixed Layer 11-12 Å			Illite 10 Å			Kaolinite + Chlorite 7.1 Å		
		2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM
0-5	Aeh	ND	ND	ND	13.64	77	1.60	11.35	63	1.05	10.11	220	0.77	7.14	266	0.64
5-10	Ah-Bv	ND	ND	ND	14.11	118	1.08	11.87	57	1.14	10.18	130	0.86	7.19	201	0.72
10-25	Bv	ND	ND	ND	14.13	202	0.52	12.36	55	1.37	10.12	162	0.84	7.16	420	0.70
25-45	IIBv	ND	ND	ND	14.11	279	0.34	12.10	59	2.64	9.97	635	0.32	7.09	547	0.58
45-65	IIBv	NA	NA	NA	14.27	514	0.25	12.10	73	0.93	10.04	1506	0.25	7.14	836	0.44
65-85	IIIBvCv	NA	NA	NA	14.18	290	0.24	12.10	72	0.8	10.01	833	0.26	7.11	512	0.47
85-100+	IViCv	NA	NA	NA	14.09	692	0.24	12.15	74	1.31	9.96	2278	0.26	7.07	1459	0.28

Note: ND= Non-Detectable
NA= Non-Applicable

Profile 4: Geinsheim

Table E.4: First Order Reflections and Response to Glycolation for the Geinsheim Profile

Depth (cm)	Horizon	Smectite 16-17 Å (glycolated)			Smectite 14.5 Å			Mixed Layer 11-12 Å			Illite 10 Å			Kaolinite + Chlorite 7.1 Å		
		2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	FWHM	2θ	I	I
0-5	Ap	16.04	496	1.99	14.22	673	1.84	11.34	140	0.97	10.15	185	0.77	7.16	463	0.43
5-10	Ap	15.77	304	1.48	14.55	582	1.58	12.00	184	1.37	10.16	216	1.03	7.19	450	0.39
10-25	Ap	15.63	419	1.52	14.25	688	1.91	11.44	109	0.94	10.12	172	0.84	7.15	451	0.41
25-50	M	16.03	541	1.46	14.55	776	1.36	11.55	115	0.98	10.17	219	0.84	7.16	405	0.44
50-70	M	16.53	599	1.44	14.30	804	1.65	11.65	124	1.19	10.27	85	0.85	7.19	410	0.45
70-90	IIP	16.60	979	1.44	14.49	1182	1.56	11.54	129	0.95	10.30	87	0.48	7.16	461	0.39
90-110	IIIfAxh-Go1	16.34	704	1.54	14.48	1010	1.20	12.24	245	1.37	10.32	55	0.90	7.16	445	0.41
110-130	IIIfAxh-Gco2	16.35	148	1.39	14.5	260	1.04	12.38	72	1.36	10.41	24	0.93	7.14	178	0.42
130-150+	IVGcro4	16.08	140	1.5	14.49	202	1.06	12.15	64	1.29	10.05	40	0.83	7.14	171	0.46

Profile 5: Frankfurter Stadtwald

Table E.5: First Order Reflections and Response to Glycolation for the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	Smectite 16-17 Å (glycolated)			Smectite 14.5 Å			Mixed Layer 11-12 Å			Illite 10 Å			Kaolinite + Chlorite 7.1 Å		
		2θ	I	FWHM	2θ	I	FWHM	2	I	FWHM	2θ	I	FWHM	2θ	I	FWHM
0-5	Ah	17.83	150	0.74	14.43	209	1.59	12.08	348	1.84	10.17	464	1.12	7.18	259	0.48
5-10	Ah	16.61	104	1.318	14.03	159	1.60	11.63	220	2.09	10.42	226	1.22	7.17	224	0.41
10-15	Ah-Go	16.60	156	0.976	14.46	312	1.41	12.24	392	1.78	10.22	169	1.13	7.19	289	0.42
15-20	Ah-Go	16.71	189	1.16	14.57	340	1.45	12.32	436	1.75	10.19	188	1.18	7.18	301	0.40
20-25	Ah-Go	16.72	320	1.07	14.59	484	1.47	12.29	661	1.81	10.23	342	1.29	7.17	427	0.46
25-30	Go	16.81	321	1.07	14.58	514	1.46	12.28	619	1.81	10.32	301	1.37	7.17	403	0.44
30-40	Go	17.07	429	1.07	14.95	670	1.60	12.28	537	1.97	10.38	339	1.35	7.19	359	0.48
40-50	Gro1	16.52	551	1.38	14.86	761	1.50	12.22	544	1.81	10.15	426	1.20	7.18	386	0.55
50-60	Gro2	16.72	884	1.09	14.86	1303	1.48	12.31	842	1.77	10.05	479	1.20	7.11	427	0.47
60-70	Gro2	17.08	672	1.02	15.08	721	1.55	12.17	328	1.84	10.17	266	1.18	7.16	243	0.47
70-80	Gro3	16.59	677	1.18	14.84	892	1.44	12.27	664	1.78	10.13	545	1.09	7.16	455	0.44
80-85	Gro3	16.69	431	1.21	14.64	780	1.38	12.19	635	1.71	10.16	505	1.16	7.16	453	0.47
85-90	IIGr	17.20	282	1.10	14.74	542	1.46	12.11	497	1.75	10.16	502	1.16	7.18	423	0.52
90-100	IIGr	16.79	445	1.09	14.67	624	1.39	12.25	647	1.67	10.12	712	1.15	7.17	652	0.51
100-110	IIGr	16.52	290	1.23	14.72	408	1.50	12.16	418	1.78	10.07	603	1.20	7.17	427	0.58

Mineral Composition of the Clay Fraction (<2 µm)

Profile 1: Münden 1

Table E.6: Mineral Composition (%) of the <2 µm Clay Fraction from the Münden 1 Profile

Depth (cm)	Vermiculite (+ Chlorite)	Mixed Layer	Illite	Chlorite	Kaolinite	Quartz	K-Feldspar	Albite	Goethite
0-5	4.9	41.5	12.9	2.7	28.2	6.5	2.1	1.2	0.0
5-10	46.6	9.7	6.4	3.0	26.4	3.9	1.6	1.5	0.8
10-20	36.1	13.0	11.1	5.6	25.7	5.3	2.0	1.3	0.0
20-30	30.1	12.3	13.1	6.6	30.4	4.1	2.1	1.3	0.0
30-60	19.1	10.0	34.7	7.3	27.1	1.9	0.0	0.0	0.0
60-80	1.3	10.4	43.6	7.1	33.5	2.0	0.0	0.0	2.0
80-100+	0.0	0.0	53.4	1.8	40.8	2.0	0.0	0.0	2.1

Profile 2: Münden 2

Table E.7: Mineral Composition (%) of the <2 µm Clay Fraction from the Münden 2 Profile

Depth (cm)	Vermiculite (+ Chlorite)	Mixed Layer	Illite	Chlorite	Kaolinite	Quartz	K-Feldspar	Albite	Goethite
0-5	22.6	17.4	23.2	4.4	17.8	8.9	3.7	2.0	0.0
5-10	43.6	18.2	8.0	7.3	13.5	5.1	3.0	1.3	0.0
10-20	42.9	17.7	10.4	5.9	14.7	4.3	2.9	1.1	0.0
20-50	32.9	12.6	21.2	7.2	13.1	5.0	4.1	3.5	0.4
50-70	24.7	17.5	27.8	7.0	10.0	7.1	2.8	3.1	0.0
70-90	40.0	13.6	20.9	6.0	12.1	2.9	2.0	2.4	0.0
90-110	24.0	29.2	26.9	6.7	11.1	2.1	0.0	0.0	0.0
110-140	34.4	14.5	22.3	5.2	13.1	3.7	4.6	2.3	0.0
140-160+	26.6	13.6	30.1	5.9	20.9	2.1	0.0	0.0	0.8

Profile 3: Königstein

Table E.8: Mineral Composition (%) of the <2 µm Clay Fraction from the Königstein Profile

Depth (cm)	Vermiculite (+ Chlorite)	Mixed Layer	Illite	Chlorite	Kaolinite	Quartz	K-Feldspar	Albite	Goethite
0-5	18.0	9.7	28.1	12.5	18.3	2.8	4.0	3.4	3.2
5-10	24.6	11.5	21.7	15.2	14.2	3.7	4.1	3.6	1.4
10-25	17.2	9.1	19.2	18.6	23.9	2.7	3.8	2.9	2.4
25-45	12.2	14.0	26.7	27.4	10.6	1.6	2.3	3.0	2.3
45-65	13.4	3.3	37.2	28.0	6.7	1.1	3.1	4.8	2.5
65-85	11.0	0.0	34.7	27.3	11.4	2.4	4.2	4.7	4.2
85-100+	12.4	4.0	41.8	28.5	5.5	0.8	2.3	4.0	0.7

Profile 4: Geinsheim

Table E.9: Mineral Composition (%) of the <2 µm Clay Fraction from the Geinsheim Profile

Depth (cm)	Smectite	Mixed Layer	Illite	Chlorite	Kaolinite	Quartz	K-Feldspar	Albite	Calcite
0-5	49.8	26.0	7.4	3.8	9.0	1.0	1.3	1.7	0.0
5-10	24.1	45.2	14.5	3.0	8.8	1.0	2.0	1.4	0.0
10-25	31.3	45.2	7.8	3.7	7.9	1.2	1.6	1.3	0.0
25-50	46.5	31.6	6.3	3.9	9.3	1.1	1.4	0.0	0.0
50-70	47.7	35.0	4.0	2.5	8.9	1.0	1.0	0.0	0.0
70-90	58.6	28.0	1.7	2.0	7.1	1.0	1.0	0.7	0.0
90-110	54.7	28.4	2.6	5.4	5.4	1.5	0.2	0.0	1.9
110-140	26.5	28.8	3.6	5.4	6.2	2.3	0.0	0.0	27.2
140-160+	28.6	20.8	6.2	7.0	6.1	2.6	0.0	0.0	28.6

Profile 5: Frankfurter Stadtwald

Table E.10: Mineral Composition (%) of the <2 µm Clay Fraction from the Frankfurter Stadtwald Profile

Depth (cm)	Smectite	Mixed Layer	Illite	Chlorite	Kaolinite	Quartz	K-Feldspar	Albite	Goethite
0-5	5.8	48.4	34.2	2.6	3.5	0.8	4.5	0.0	0.3
5-10	10.9	48.7	26.0	3.2	4.9	1.8	4.6	0.0	0.0
10-15	9.3	63.0	14.0	2.2	6.5	1.4	3.6	0.0	0.0
15-20	12.0	58.0	14.8	2.6	6.6	1.2	3.3	1.3	0.0
20-25	11.8	55.6	18.2	2.5	6.8	0.4	3.4	1.4	0.0
25-30	12.1	58.1	16.8	2.2	5.9	0.6	4.3	0.0	0.0
30-40	14.9	55.7	16.6	3.1	4.3	0.4	3.9	1.1	0.0
40-50	22.7	44.6	19.8	1.7	4.8	0.4	4.8	1.2	0.0
50-60	21.4	54.8	15.1	2.3	2.9	0.3	3.3	0.0	0.0
60-70	29.9	45.2	15.3	1.7	4.4	0.2	3.3	0.0	0.0
70-80	22.5	47.9	19.6	1.7	4.7	0.3	3.2	0.0	0.0
80-85	15.9	52.5	21.0	1.9	5.2	0.6	2.9	0.0	0.0
85-90	10.8	50.6	24.4	3.0	5.9	0.3	2.6	2.4	0.0
90-100	12.9	44.5	27.5	3.4	7.8	0.2	3.6	0.0	0.0
100-110	12.8	38.8	33.0	4.8	7.9	0.3	2.4	0.0	0.0

Appendix F: Examples of X-ray Diffraction Patterns for Each Profile

Profile 1: Münden 1

Figure F.1: XRD Pattern for 5-10 cm from the Münden 1 Profile

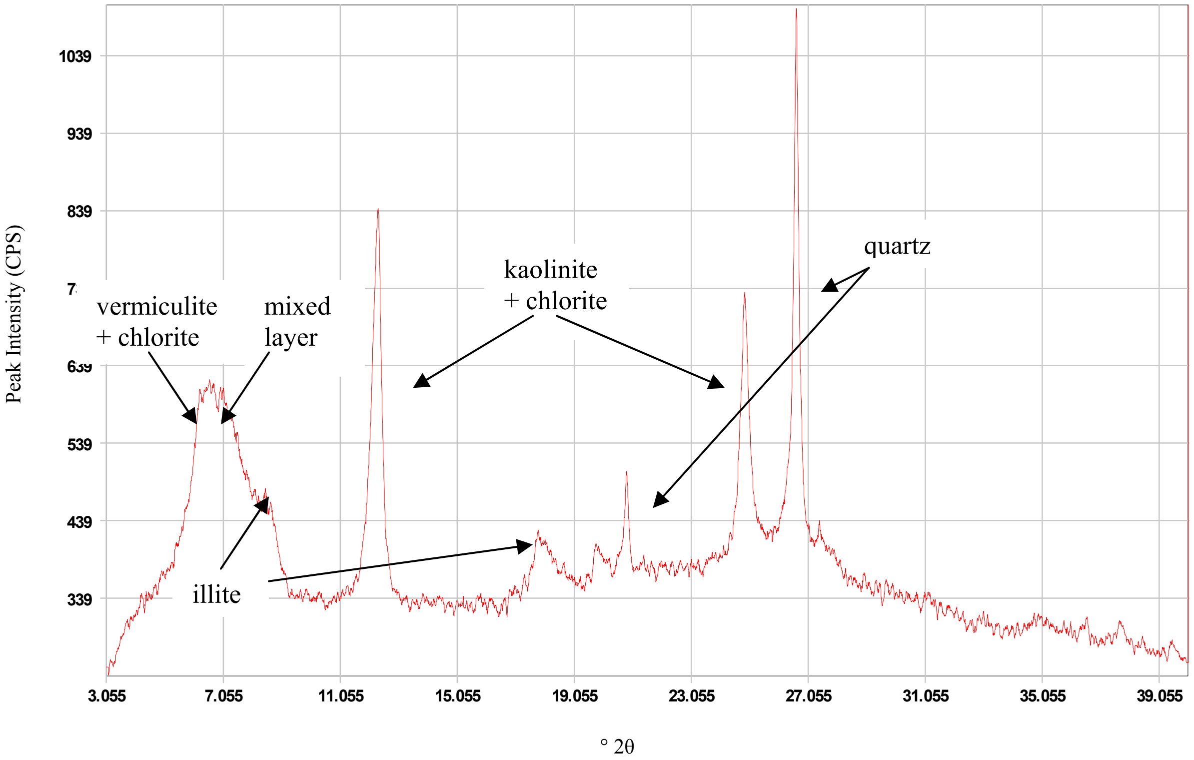
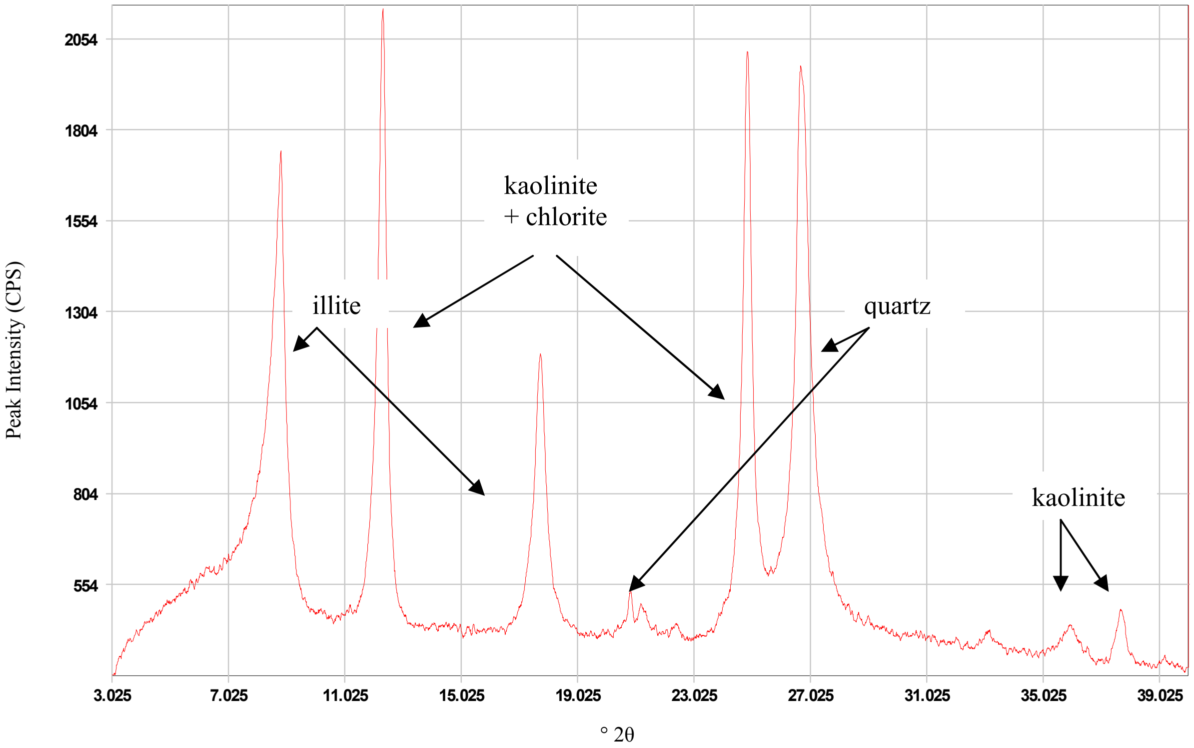


Figure F.2: XRD Pattern for 80-100 cm from the Münden 1 Profile



Profile 2: Münden 2

Figure F.3: XRD Pattern for 5-10 cm from the Münden 2 Profile

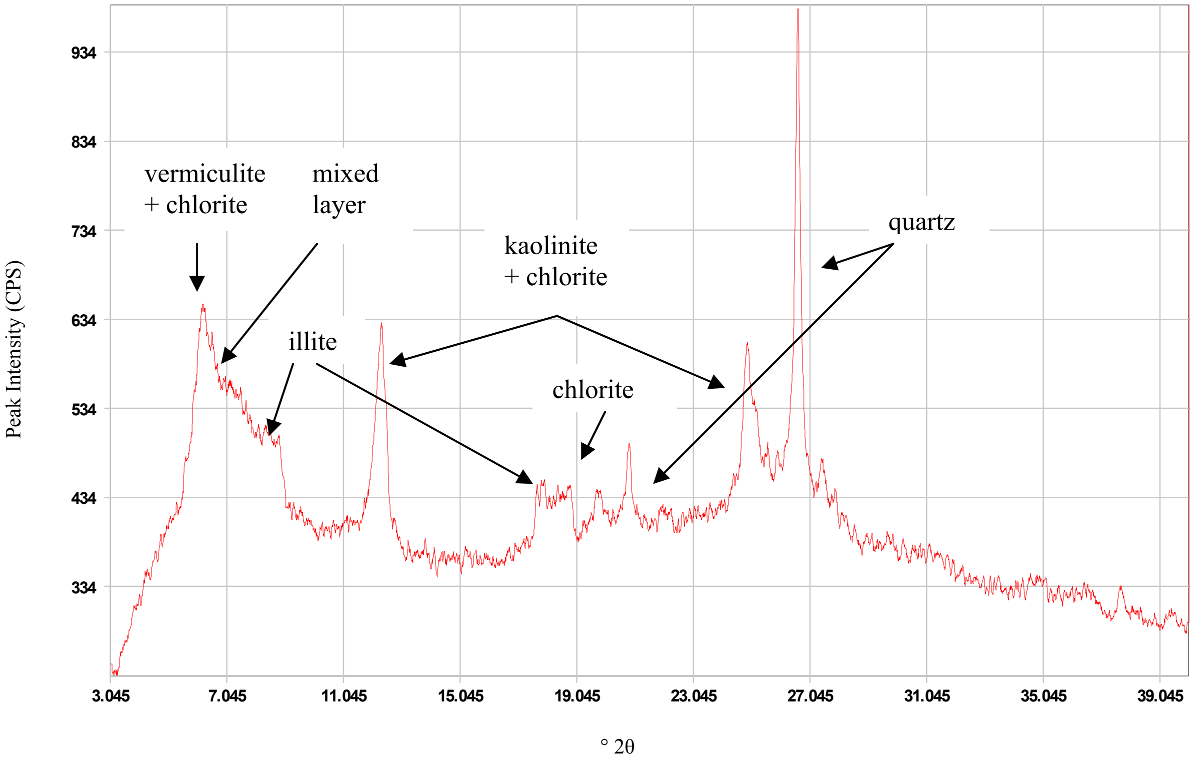
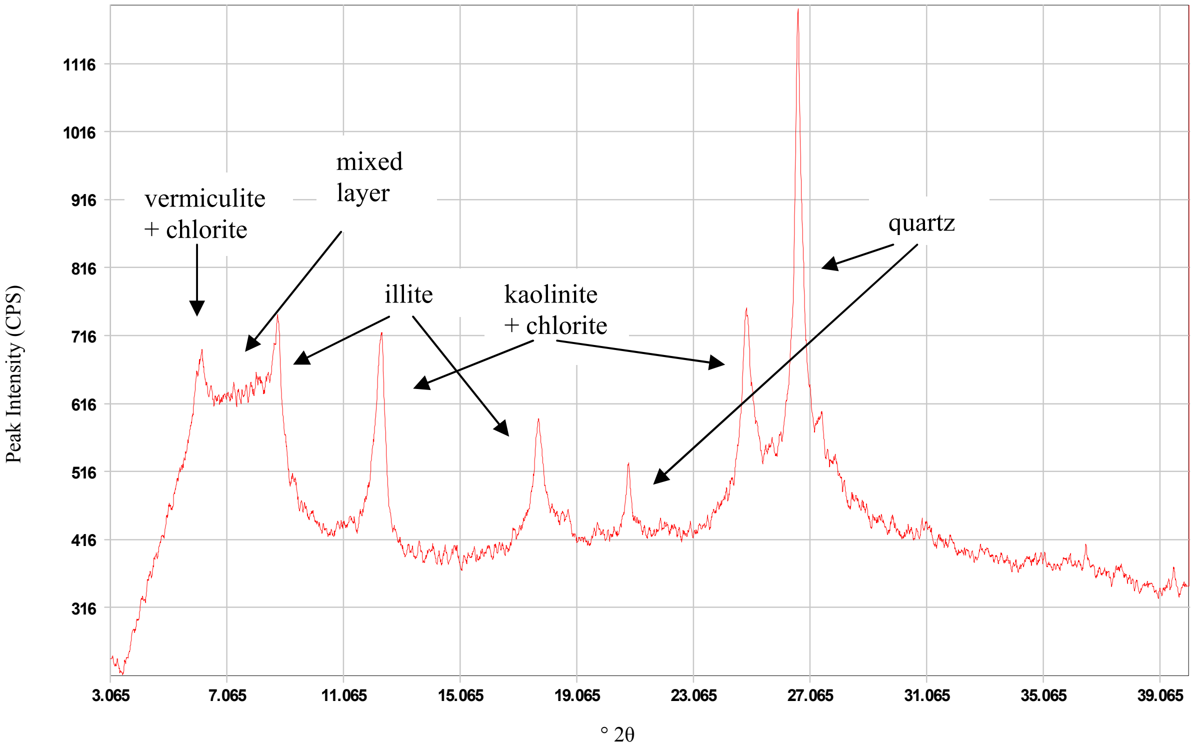


Figure F.4: XRD Pattern for 110-140 cm from the Münden 2 Profile



Profile 3: Königstein

Figure F.5: XRD Pattern for 0-5 cm from the Königstein Profile

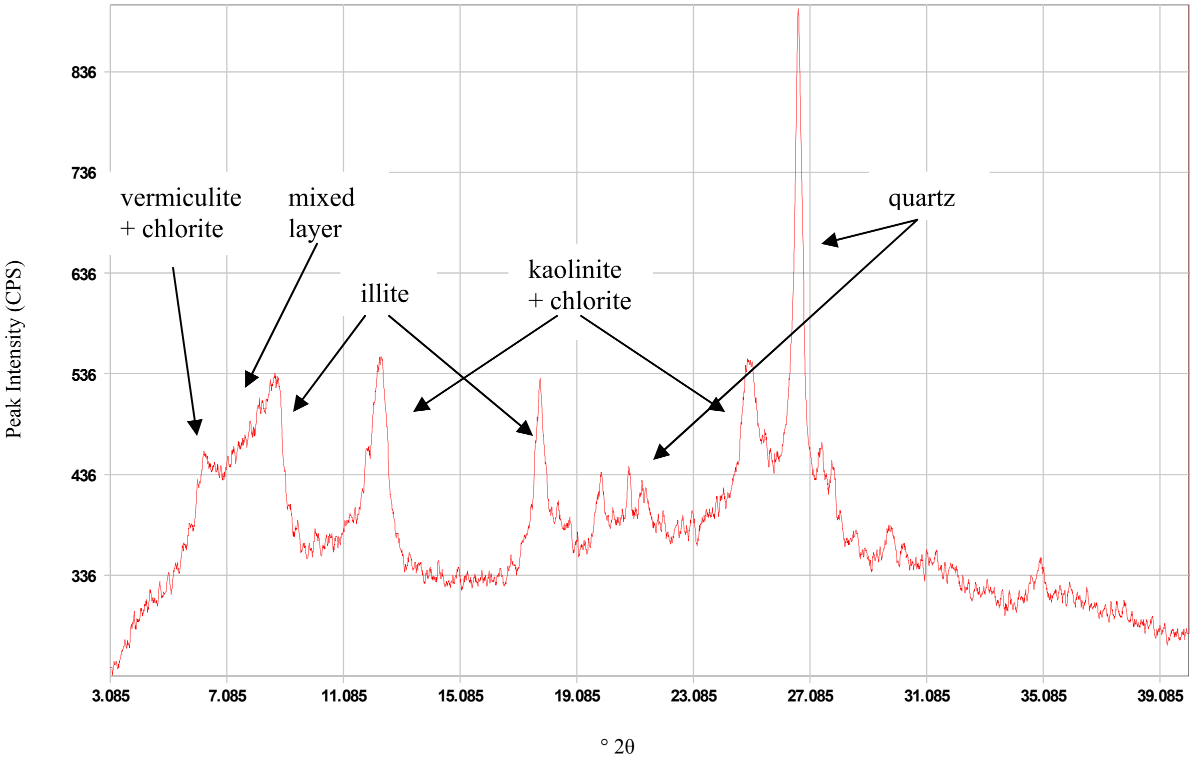
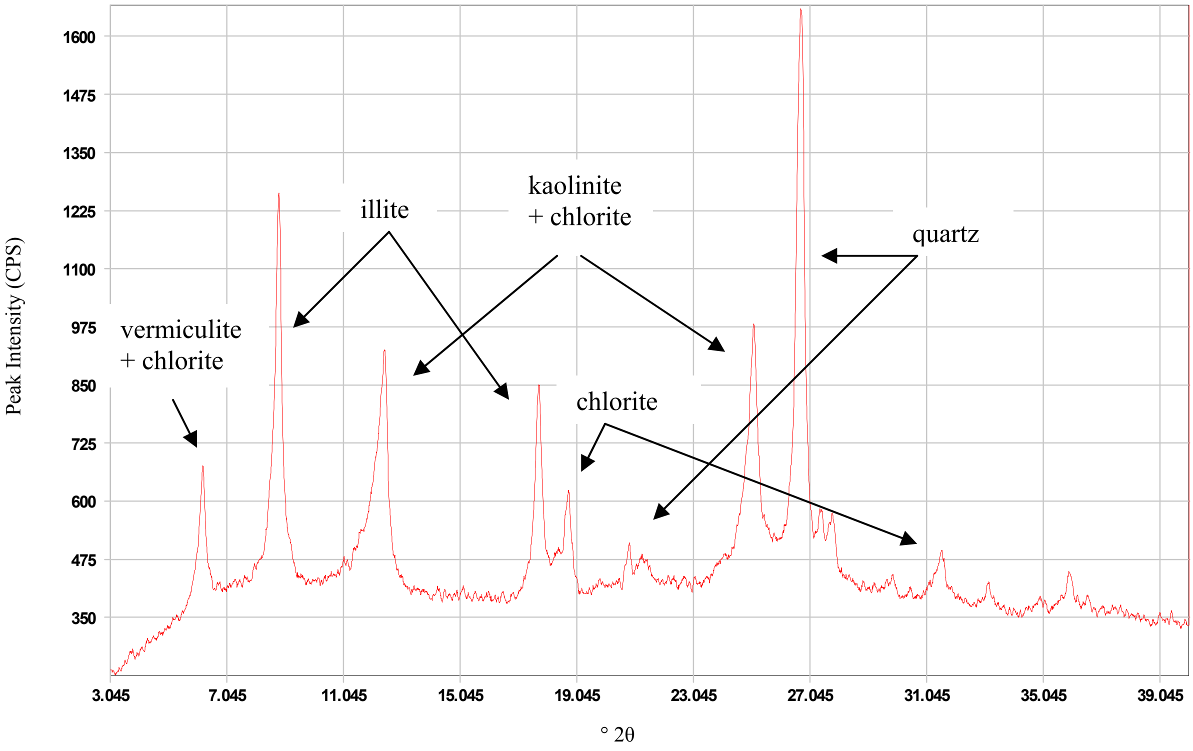


Figure F.6: XRD Pattern for 65-85 cm from the Königstein Profile



Profile 4: Geinsheim

Figure F.7: XRD Pattern for 5-10 cm from the Geinsheim Profile

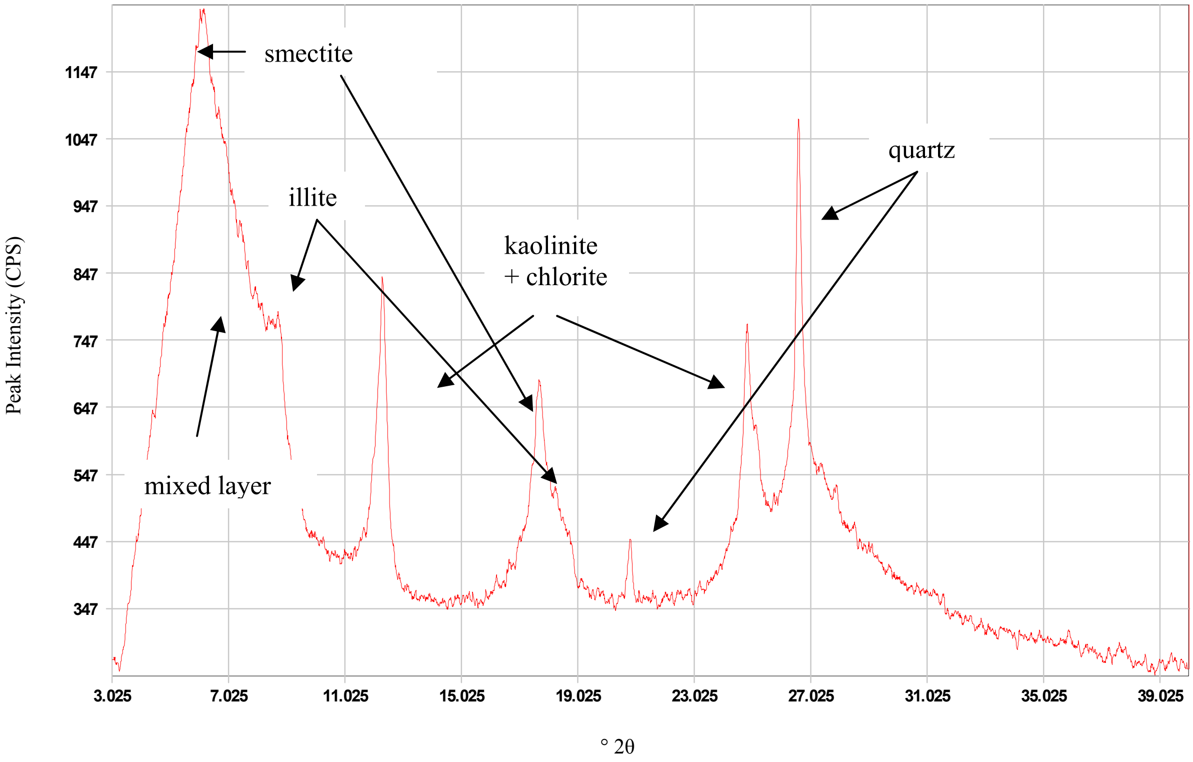
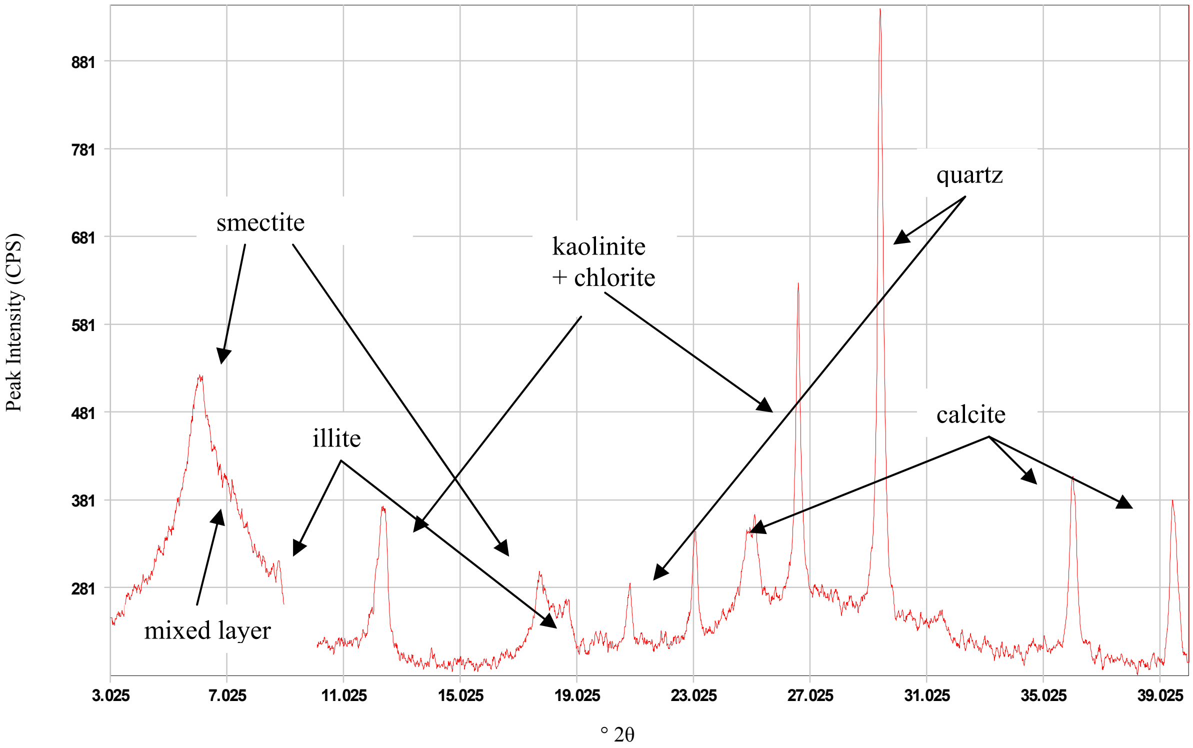


Figure F.8: XRD Pattern for 130-150 cm from the Geinsheim Profile



Profile 5: Frankfurter Stadtwald

Figure F.9: XRD Pattern for 0-5 cm from the Frankfurter Stadtwald Profile

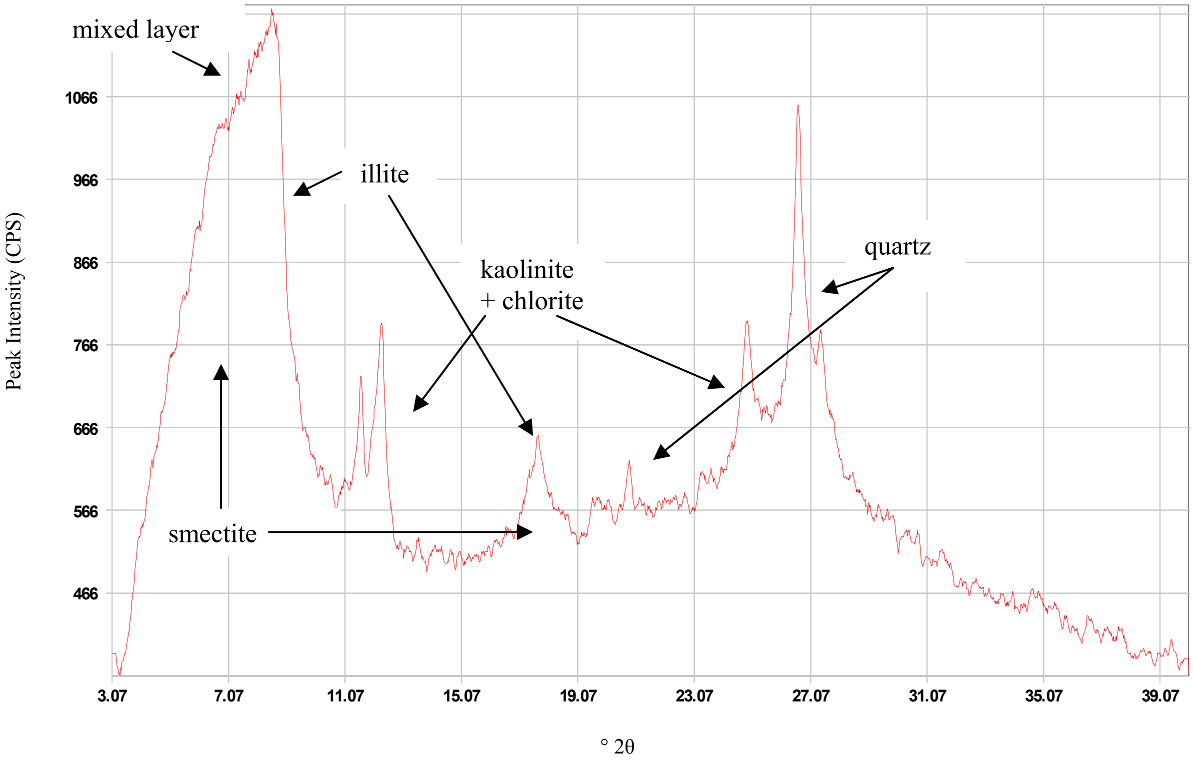
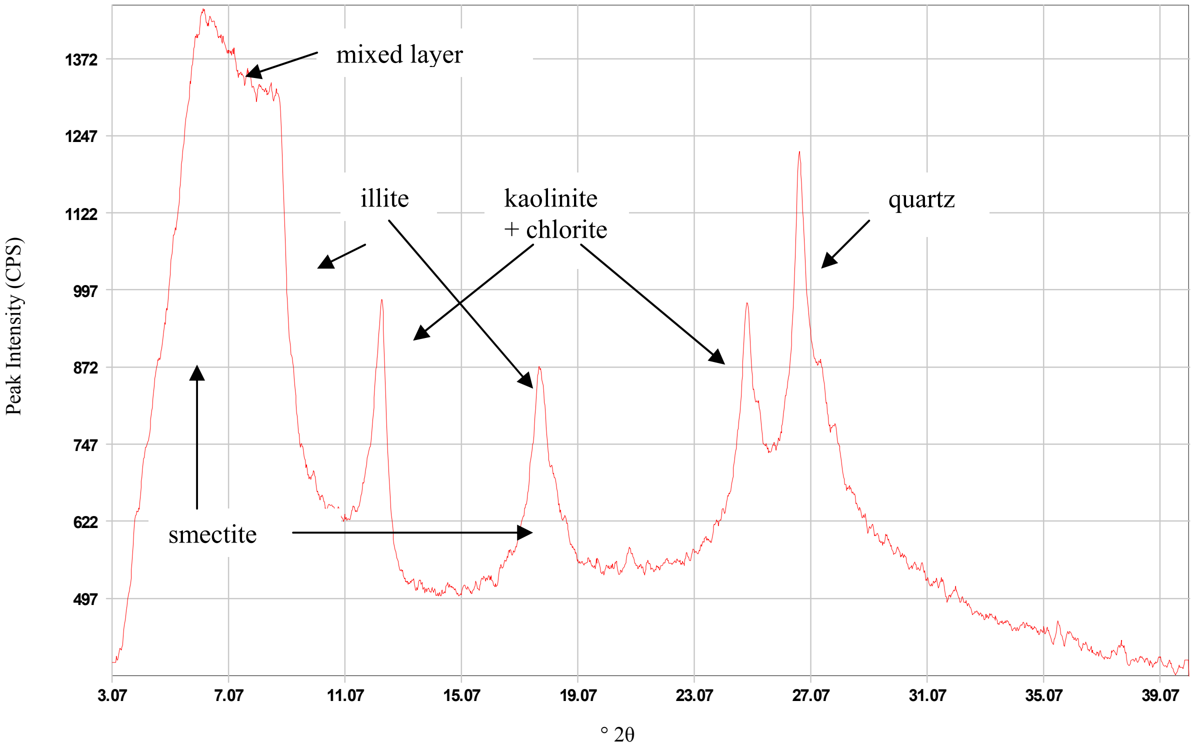


Figure F.10: XRD Pattern for 85-95 cm from the Frankfurter Stadtwald Profile



Appendix G: Specific Surface Area for the Silt and Clay Size Fractions

Profile 1: Münden 1

Table G.1: Specific Surface Area ($m^2\ g^{-1}$) for the Silt and Clay Size Fractions (<63 µm) from the Münden 1 Profile

Depth (cm)	Horizon	Fraction (µm)	Specific Surface Area ($m^2\ g^{-1}$)
0-5	Aeh	<63	NA
		<20	15
		<6.3	28
		<2	NA
		<1	63
5-10	Ahe-Bv	<63	11
		<20	24
		<6.3	44
		<2	56
		<1	113
10-20	Ah-Bv	<63	23
		<20	24
		<6.3	NA
		<2	NA
		<1	163
20-30	Bv	<63	NA
		<20	39
		<6.3	63
		<2	93
		<1	164
30-60	sBv	<63	47
		<20	57
		<6.3	103
		<2	NA
		<1	171
60-80	IIBvCv	<63	56
		<20	92
		<6.3	138
		<2	175
		<1	175
80-100+	IIiICv	<63	48
		<20	54
		<6.3	87
		<2	118
		<1	105

Note: NA= Non-Applicable

Profile 2: Münden 2

Table G.2: Specific Surface Area ($m^2 g^{-1}$) for the Silt and Clay Size Fractions (<63 µm) from the Münden 2 Profile

Depth (cm)	Horizon	Fraction (µm)	Specific Surface Area ($m^2 g^{-1}$)
0-5	Ah	<63	NA
		<20	NA
		<6.3	NA
		<2	84
		<1	106
5-10	Al	<63	20
		<20	30
		<6.3	94
		<2	119
		<1	146
10-20	Al	<63	42
		<20	82
		<6.3	125
		<2	171
		<1	255
20-50	Sw-Al	<63	NA
		<20	103
		<6.3	157
		<2	155
		<1	238
50-70	Sd-Bt	<63	84
		<20	120
		<6.3	NA
		<2	NA
		<1	NA
70-90	sBtv	<63	130
		<20	213
		<6.3	211
		<2	268
		<1	336
90-110	sBv	<63	69
		<20	129
		<6.3	142
		<2	225
		<1	295
110-140	IIiIsCv	<63	32
		<20	110
		<6.3	136
		<2	192
		<1	296
140-160+	IIiICv	<63	79
		<20	116
		<6.3	180
		<2	224
		<1	296

Note: NA= Non-Applicable

Profile 3: Königstein

Table G.3: Specific Surface Area ($m^2 g^{-1}$) for the Silt and Clay Size Fractions (<63 µm) from the Königstein Profile

Depth (cm)	Horizon	Fraction (µm)	Specific Surface Area ($m^2 g^{-1}$)
0-5	Aeh	<63	39
		<20	37
		<6.3	NA
		<2	NA
		<1	75
5-10	Ah-Bv	<63	35
		<20	49
		<6.3	75
		<2	82
		<1	94
10-25	Bv	<63	31
		<20	46
		<6.3	64
		<2	85
		<1	100
25-45	IIBv	<63	44
		<20	43
		<6.3	68
		<2	94
		<1	110
45-65	IIBv	<63	47
		<20	51
		<6.3	59
		<2	74
		<1	81
65-85	IIIBvCv	<63	45
		<20	50
		<6.3	43
		<2	51
		<1	76
85-100+	IViCv	<63	34
		<20	36
		<6.3	40
		<2	59
		<1	96

Note: NA= Non-Applicable

Profile 4: Geinsheim

Table G.4: Specific Surface Area ($m^2 g^{-1}$) for the Silt and Clay Size Fractions (<63 µm) from the Geinsheim Profile

Depth (cm)	Horizon	Fraction (µm)	Specific Surface Area ($m^2 g^{-1}$)
0-5	Ap	<63	215
		<20	235
		<6.3	231
		<2	317
		<1	346
5-10	Ap	<63	221
		<20	244
		<6.3	278
		<2	326
		<1	353
10-25	Ap	<63	237
		<20	244
		<6.3	268
		<2	318
		<1	341
25-50	M	<63	246
		<20	258
		<6.3	307
		<2	348
		<1	385
50-70	M	<63	235
		<20	262
		<6.3	260
		<2	326
		<1	374
70-90	IIP	<63	251
		<20	279
		<6.3	271
		<2	380
		<1	414
90-110	IIIfAxh-Go1	<63	236
		<20	253
		<6.3	331
		<2	417
		<1	400
110-130	IIIfAxh-Go2	<63	164
		<20	202
		<6.3	208
		<2	287
		<1	318
130-150+	IVGro4	<63	109
		<20	138
		<6.3	211
		<2	285
		<1	253

Note: NA= Non-Applicable

Profile 5: Frankfurter Stadtwald

Table G.5: Specific Surface Area ($m^2\ g^{-1}$) for the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	Fraction (µm)	Specific Surface Area ($m^2\ g^{-1}$)
0-5	Ah	<63	116
		<20	117
		<6.3	152
		<2	140
5-10	Ah	<63	119
		<20	98
		<6.3	NA
		<2	NA
10-15	AhGo	<63	158
		<20	166
		<6.3	216
		<2	213
15-20	AhGo	<63	153
		<20	180
		<6.3	215
		<2	265
20-25	AhGo	<63	199
		<20	243
		<6.3	266
		<2	296
25-30	Go1	<63	223
		<20	234
		<6.3	290
		<2	339
30-40	Go2	<63	218
		<20	267
		<6.3	300
		<2	346
40-50	Gro1	<63	220
		<20	248
		<6.3	328
		<2	352
50-60	Gro2	<63	258
		<20	285
		<6.3	342
		<2	376
60-70	Gro2	<63	NA
		<20	263
		<6.3	319
		<2	373
70-80	Gro3	<63	210
		<20	220
		<6.3	266
		<2	337
80-85	Gro3	<63	163
		<20	208
		<6.3	249
		<2	331

Table G.5 (continued): Specific Surface Area (m^2 g^{-1}) for the Silt and Clay Size Fractions (<63 µm) from the Frankfurter Stadtwald Profile

85-90	IIGr	<63	200
		<20	241
		<6.3	262
		<2	305
90-100	IIGr	<63	196
		<20	236
		<6.3	274
		<2	310
100-110	IIGr	<63	186
		<20	211
		<6.3	238
		<2	274

Note: NA= Non-Applicable

Appendix H: Dithionite- and Oxalate-Extractable Fe, Al and Mn

Profile 1: Münden 1

Table H.1: Dithionite-Extractable Fe (Fed) and Oxalate-Extractable Fe (Feo), Al (Alo) and Mn (Mno) in Bulk Soil Samples (<2 mm) from the Münden 1 Profile

Depth (cm)	Horizon	µ Fed (mg g^{-1})	µ Feo (mg g^{-1})	µ Alo (mg g^{-1})	µ Mno (mg g^{-1})
0-5	Aeh	5.325	2.613	1.405	0.009
5-10	Ahe-Bv	7.200	4.199	1.192	0.004
10-20	Ah-Bv	5.988	3.285	1.754	0.006
20-30	Bv	5.203	2.136	1.709	0.008
30-60	sBv	8.140	1.622	1.248	0.007
60-80	IIBvCv	11.597	1.146	1.013	0.003
80-100+	IIiICv	13.175	0.692	0.654	0.002

Profile 2: Münden 2

Table H.2: Dithionite-Extractable Fe (Fed) and Oxalate-Extractable Fe (Feo), Al (Alo) and Mn (Mno) in Bulk Soil Samples (<2 mm) from the Münden 2 Profile

Depth (cm)	Horizon	µ Fed (mg g^{-1})	µ Feo (mg g^{-1})	µ Alo (mg g^{-1})	µ Mno (mg g^{-1})
0-5	Ah	5.876	2.374	0.800	0.038
5-10	Al	6.239	2.853	1.410	0.030
10-20	Al	5.736	1.993	1.367	0.061
20-50	Sw-Al	6.853	1.467	1.509	0.134
50-70	Sd-Bt	8.185	1.556	1.564	0.168
70-90	sBtv	7.722	1.620	1.265	0.198
90-110	sBv	8.400	1.653	1.058	0.165
110-140	IIiIsCv	8.206	1.402	0.767	0.192
140-160+	IIiICv	8.339	1.278	0.681	0.204

Profile 3: Königstein

Table H.3: Dithionite-Extractable Fe (Fed) and Oxalate-Extractable Fe (Feo), Al (Alo) and Mn (Mno) in Bulk Soil Samples (<2 mm) from the Königstein Profile

Depth (cm)	Horizon	µ Fed (mg g^{-1})	µ Feo (mg g^{-1})	µ Alo (mg g^{-1})	µ Mno (mg g^{-1})
0-5	Aeh	10.229	3.093	1.919	0.278
5-10	Ah-Bv	10.258	3.394	2.194	0.243
10-25	Bv	11.612	2.499	2.334	0.787
25-45	IIBv	11.914	1.533	1.359	0.642
45-65	IIBv	14.977	1.044	1.035	0.372
65-85	IIIBvCv	14.228	1.188	1.086	0.390
85-100+	IViCv	10.121	0.861	0.736	0.171

Profile 4: Geinsheim

Table H.4: Dithionite-Extractable Fe (Fed) and Oxalate-Extractable Fe (Feo), Al (Alo) and Mn (Mno) in Bulk Soil Samples (<2 mm) from the Geinsheim Profile

Depth (cm)	Horizon	µ Fed (mg g^{-1})	µ Feo (mg g^{-1})	µ Alo (mg g^{-1})	µ Mno (mg g^{-1})
0-5	Ap	7.225	1.349	1.343	0.287
5-10	Ap	7.594	1.508	1.372	0.306
10-25	Ap	6.829	1.368	1.324	0.292
25-50	M	6.227	1.402	1.180	0.272
50-70	M	7.687	1.743	1.518	0.233
70-90	IIP	7.540	0.556	1.508	0.144
90-110	IIIfAxh-Go1	5.580	0.174	1.060	0.283
110-130	IIIfAxh-Gco2	2.497	0.091	0.226	0.153
130-150+	IVGcro4	1.160	0.082	0.144	0.342

Profile 5: Frankfurter Stadtwald

Table H.5: Dithionite-Extractable Fe (Fed) and Oxalate-Extractable Fe (Feo), Al (Alo) and Mn (Mno) in Bulk Soil Samples (<2 mm) from the Frankfurter Stadtwald Profile

Depth (cm)	Horizon	µ Fed (mg g^{-1})	µ Feo (mg g^{-1})	µ Alo (mg g^{-1})	µ Mno (mg g^{-1})
0-5	Ah	8.315	2.974	2.679	0.360
5-10	Ah	8.901	3.230	3.111	0.150
10-25	Ah-Go	12.261	3.630	3.216	0.434
25-40	Go	7.280	2.459	1.790	1.794
40-70	Gro1+Gro2	4.171	1.334	1.364	0.691
70-85	Gro3	1.533	0.254	0.677	0.017
85-110	IIGr	0.424	0.245	0.094	0.009

Appendix I: Soil Texture, Particle Size Separates and the OC and N Contents and C:N Ratios of Bulk Samples

Profile 1: Münden 1

No statistically significant positive relationships observed between variables for the whole soil profile.

Profile 2: Münden 2

No statistically significant positive relationships observed between variables for the whole soil profile.

Profile 3: Königstein

Figure I.1: Percent Clay vs. OC Content of Bulk Soil Samples (<2 µm) from the Königstein Profile

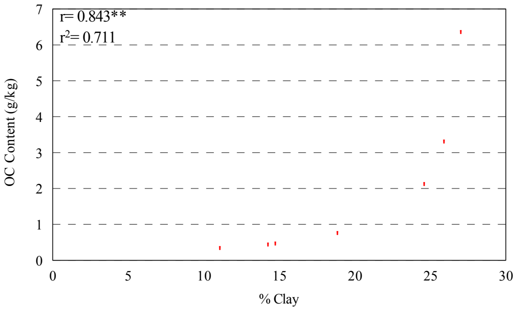


Figure I.2: Percent Clay vs. N Content of Bulk Soil Samples (<2 µm) from the Königstein Profile

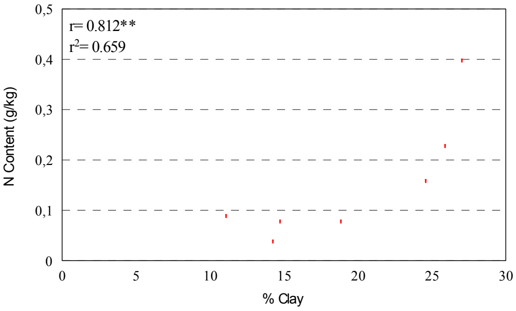
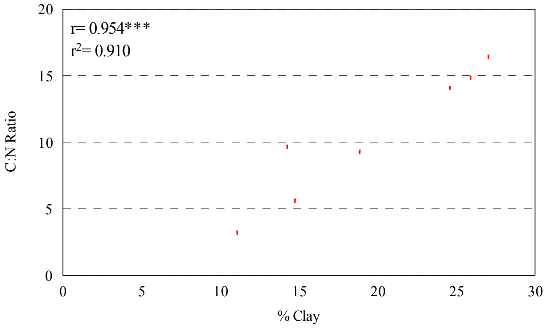
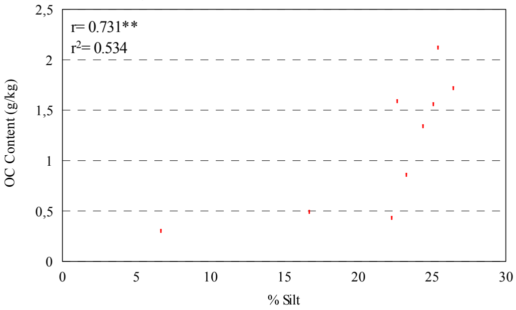


Figure I.3: Percent Clay vs. C:N Ratio of Bulk Soil Samples (<2 µm) from the Königstein Profile



Profile 4: Geinsheim

Figure I.4: Percent Silt vs. OC Content of Bulk Soil Samples (<2 µm) from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure I.5: Percent Silt vs. N Content of Bulk Soil Samples (<2 µm) from the Geinsheim Profile

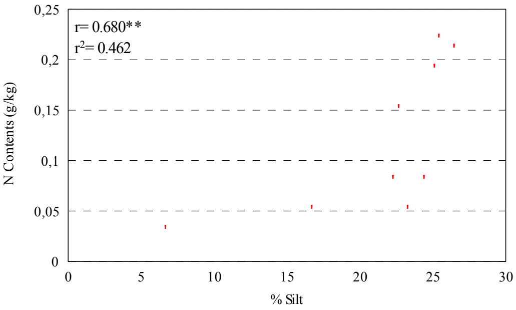


Figure I.6: Percent Clay vs. OC Content of Bulk Soil Samples (<2 µm) from the Geinsheim Profile

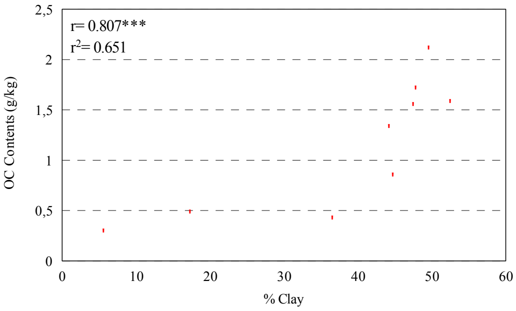
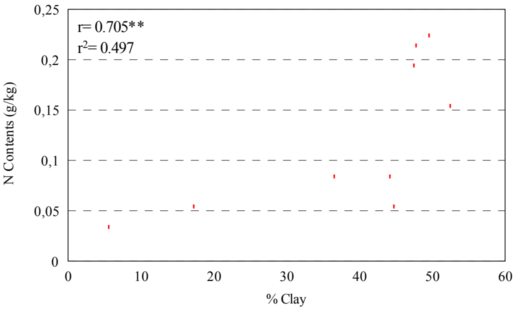


Figure I.7: Percent Clay vs. N Content of Bulk Soil Samples (<2 µm) from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 5: Frankfurter Stadtwald

No statistically significant positive relationships observed between variables for the whole soil profile

Appendix J: Clay Mineral Composition and the OC and N Contents and C:N Ratios of Clay Samples

Profile 1: Münden 1

Figure J.1: Vermiculite vs. C:N Ratio of Clay Samples (<2 µm) from the Münden 1 Profile

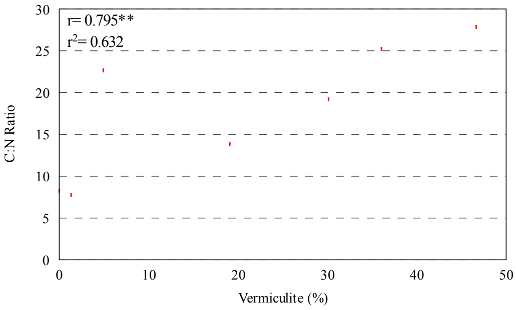


Figure J.2: Mixed Layer vs. OC Content of Clay Samples (<2 µm) from the Münden 1 Profile

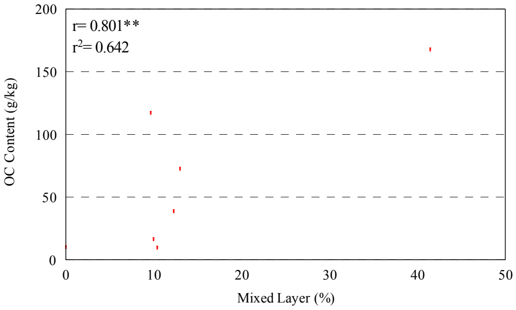
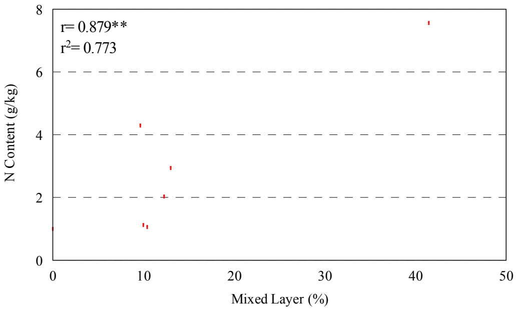


Figure J.3.: Mixed Layer vs. N Content of Clay Samples (<2 µm) from the Münden 1 Profile

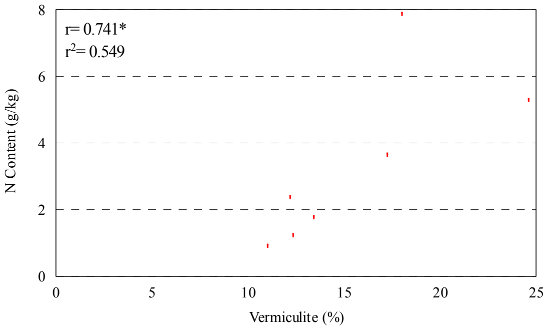


Profile 2: Münden 2

No statistically significant positive correlations observed between variables for the whole soil profile.

Profile 3: Königstein

Figure J.4: Vermiculite vs. N Content of Clay Samples (<2 µm) from the Königstein Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 4: Geinsheim

Figure J.5: Mixed Layer vs. OC Content of Clay Samples (<2 µm) from the Geinsheim Profile

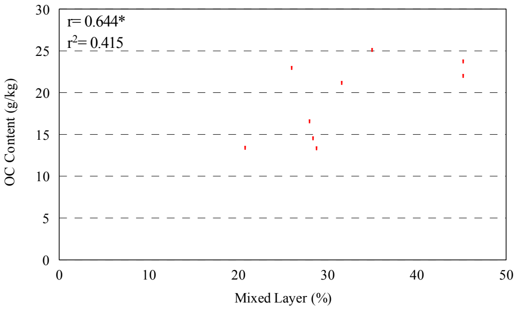


Figure J.6: Mixed Layer vs. N Content of Clay Samples (<2 µm) from the Geinsheim Profile

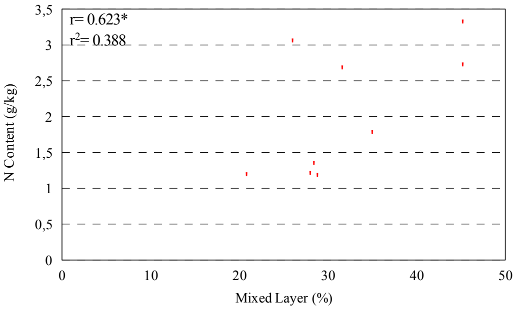


Figure J.7: Illite vs. N Content of Clay Samples (<2 µm) from the Geinsheim Profile

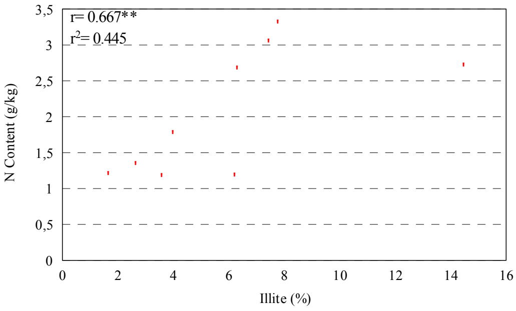


Figure J.8: Kaolinite vs. OC Content of Clay Samples (<2 µm) from the Geinsheim Profile

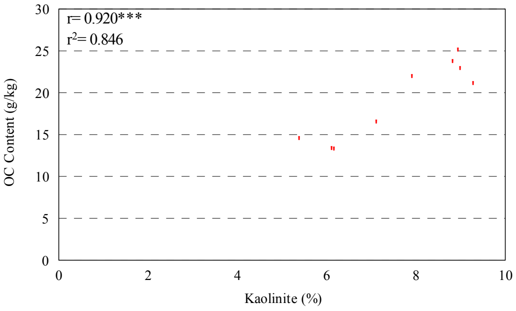
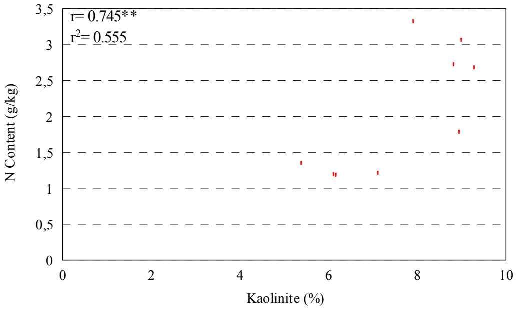


Figure J.9: Kaolinite vs. N Content of Clay Samples (<2 µm) from the Geinsheim Profile



Profile 5: Frankfurter Stadtwald

Figure J.10: Illite vs. OC Content of Clay Samples (<2 µm) from the Frankfurter Stadtwald Profile

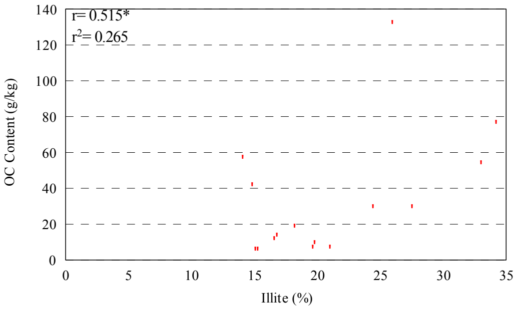
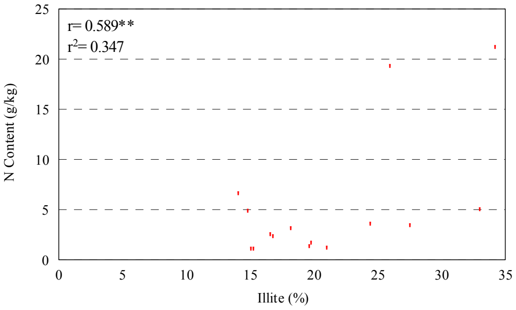


Figure J.11: Illite vs. N Content of Clay Samples (<2 µm) from the Frankfurter Stadtwald Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure J.12: Chlorite vs. C:N Ratio of Clay Samples from Frankfurter Stadtwald

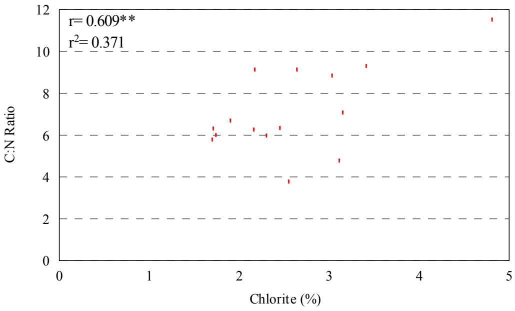
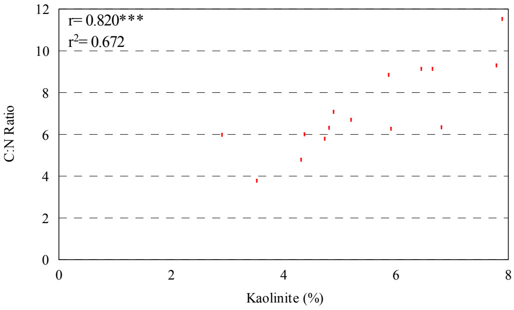


Figure J. 13: Kaolinite vs. C:N Ratio of Clay Samples from Frankfurter Stadtwald



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Appendix K: Cation Saturation and the OC and N Contents and C:N Ratios of Bulk Samples

Profile 1: Münden 1

Figure K.1: Mg vs. OC Content of Bulk Samples (<2 mm) from the Münden 1 Profile

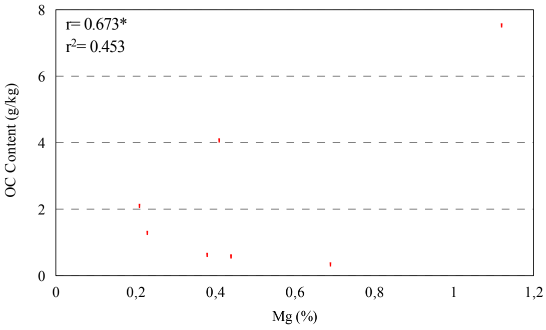


Figure K.2: Ca vs. OC Content of Bulk Samples (<2 mm) from the Münden 1 Profile

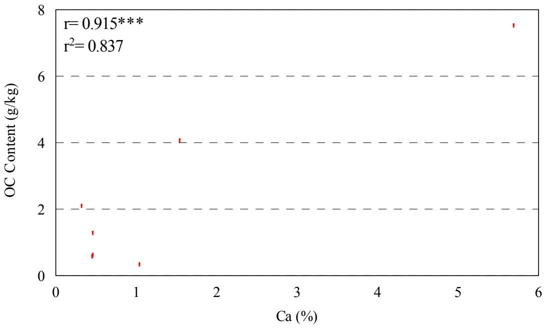


Figure K.3: Ca vs. N Content of Bulk Samples (<2 mm) from the Münden 1 Profile

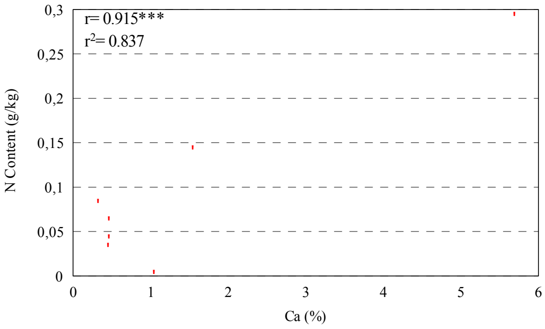


Figure K.4: Fe vs. C:N Ratio of Bulk Samples (<2 mm) from the Münden 1 Profile

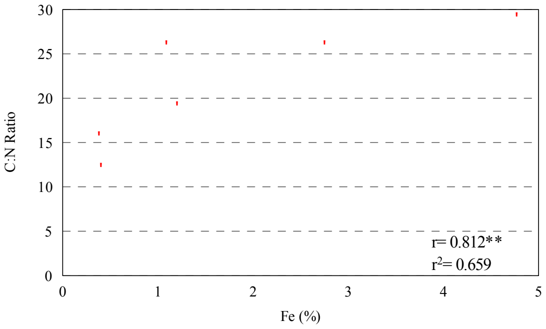


Figure K.5: H vs. OC Content of Bulk Samples (<2 mm) from the Münden 1 Profile

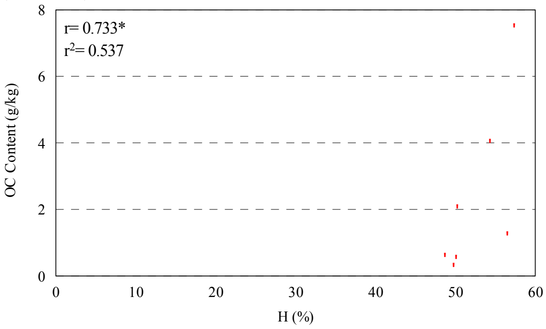
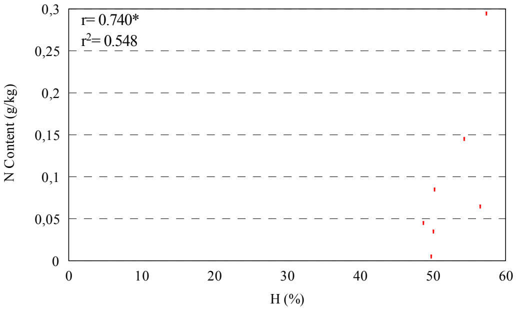


Figure K.6: H vs. N Content of Bulk Samples (<2 mm) from the Münden 1 Profile



Profile 2: Münden 2

Figure K.7: Fe vs. OC Content of Bulk Samples (<2 mm) from Münden 2

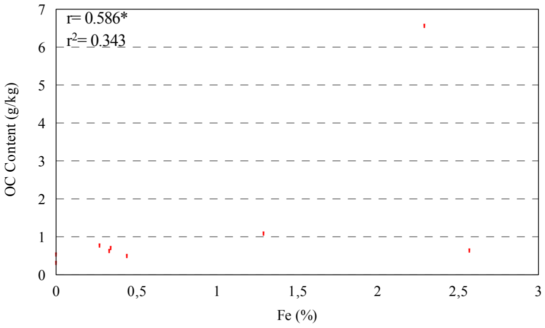
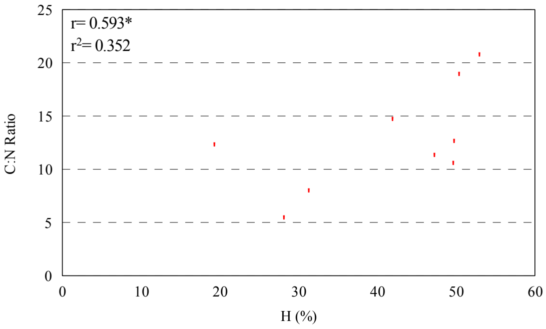


Figure K.8: H vs. C:N Ratio of Bulk Samples (<2 mm) from Münden 2



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 3: Königstein

Figure K.9: Mg vs. OC Content of Bulk Samples (<2 mm) from the Königstein Profile

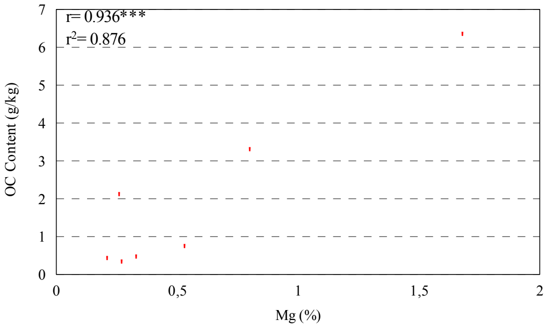


Figure K.10: Mg vs. N Content of Bulk Samples (<2 mm) from the Königstein Profile

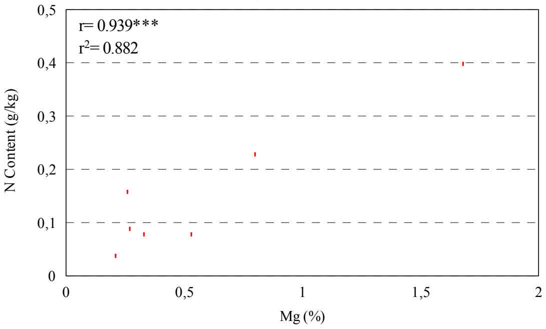


Figure K.11: Ca vs. OC Content of Bulk Samples (<2 mm) from the Königstein Profile

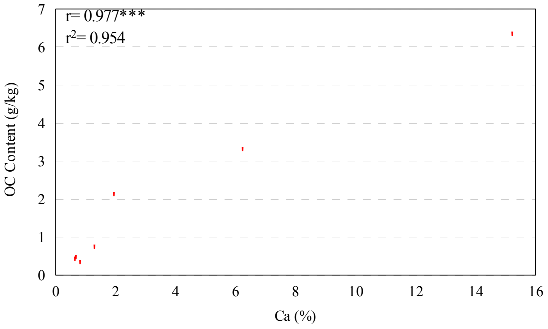


Figure K.12: Ca vs. N Content of Bulk Samples (<2 mm) from the Königstein Profile

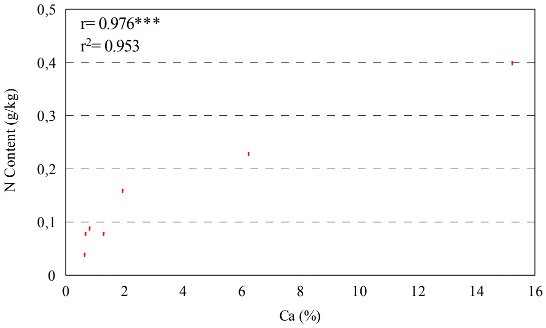


Figure K.13: Ca vs. C:N Ratio of Bulk Samples (<2 mm) from the Königstein Profile

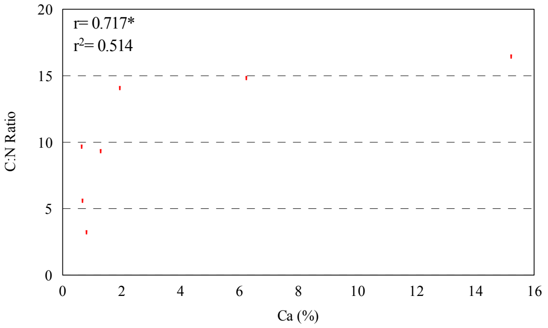


Figure K.14: Fe vs. OC Content of Bulk Samples (<2 mm) from the Königstein Profile

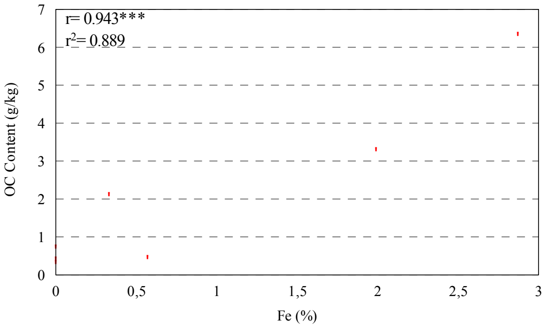


Figure K.15: Fe vs. N Content of Bulk Samples (<2 mm) from the Königstein Profile

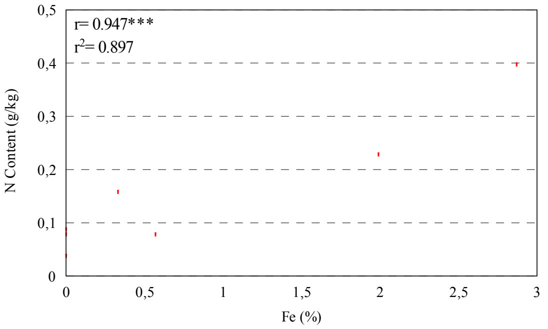
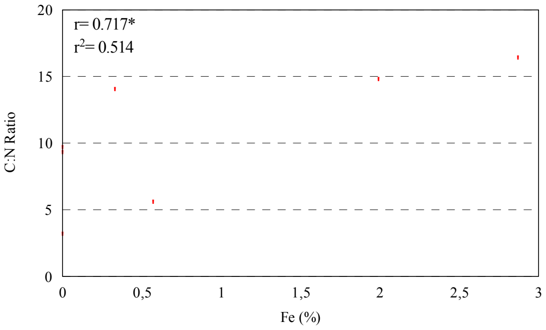


Figure K.16: Fe vs. C:N Ratio of Bulk Samples (<2 mm) from the Königstein Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure K.17: Mn vs. OC Content of Bulk Samples (<2 mm) from the Königstein Profile

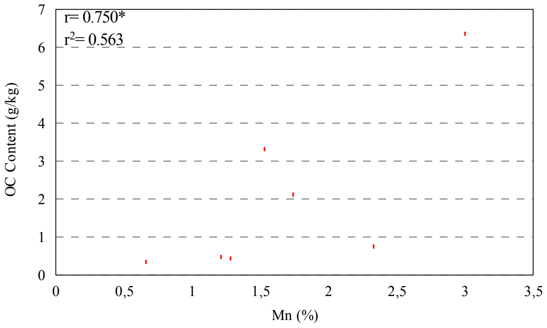


Figure K.18: Mn vs. N Content of Bulk Samples (<2 mm) from the Königstein Profile

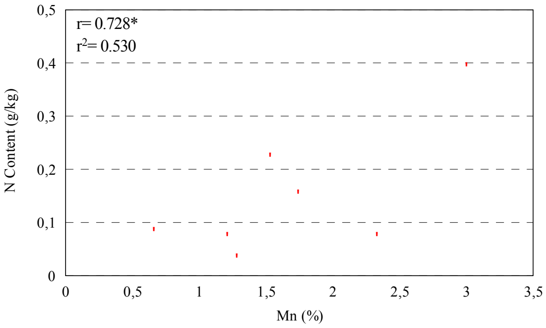
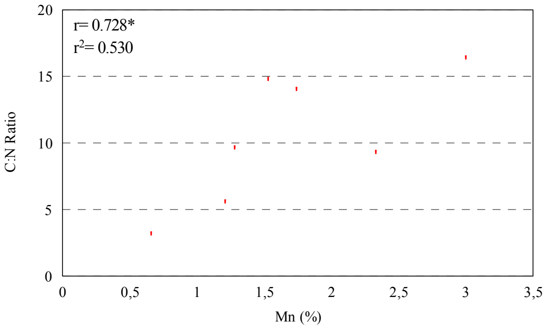


Figure K.19: Mn vs. C:N Ratio of Bulk Samples (<2 mm) from the Königstein Profile



Profile 4: Geinsheim

Figure K.20: Na vs. OC Content of Bulk Samples (<2 mm) from the Geinsheim Profile

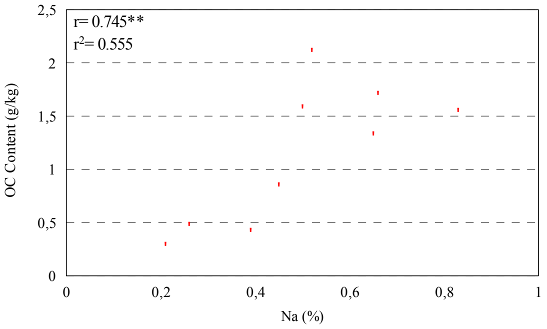


Figure K.21: Na vs. N Content of Bulk Samples (<2 mm) from the Geinsheim Profile

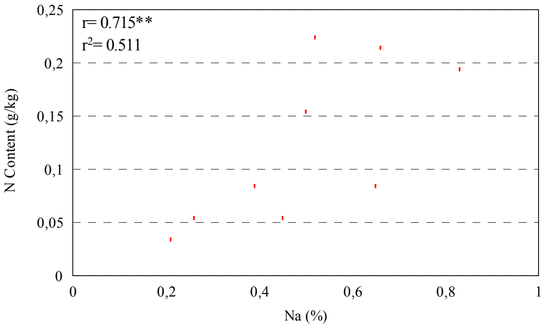


Figure K.22: K vs. OC Content of Bulk Samples (<2 mm) from the Geinsheim Profile

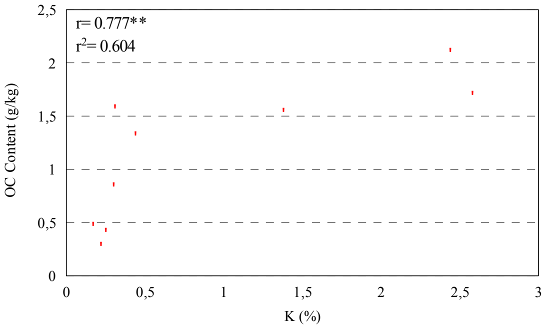
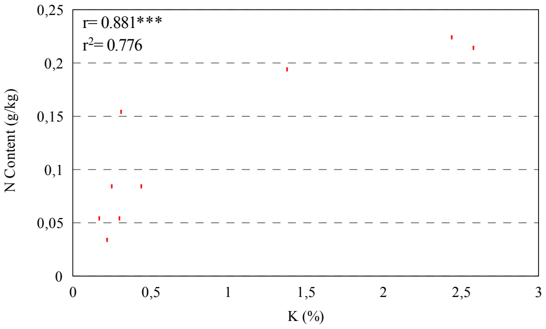


Figure K.23: K vs. N Content of Bulk Samples (<2 mm) from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Appendix L: Cation Saturation and Clay Mineral Composition

Profile 1: Münden 1

Figure L.1: K vs. Illite for the Münden 1 Profile

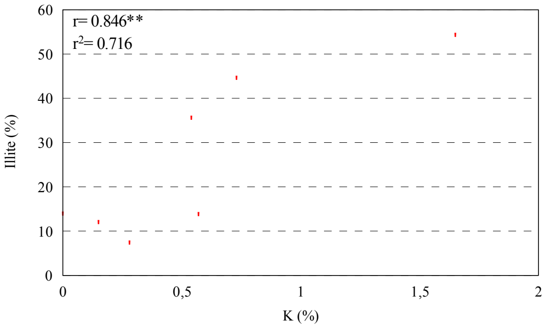


Figure L.2: K vs. Kaolinite for the Münden 1 Profile

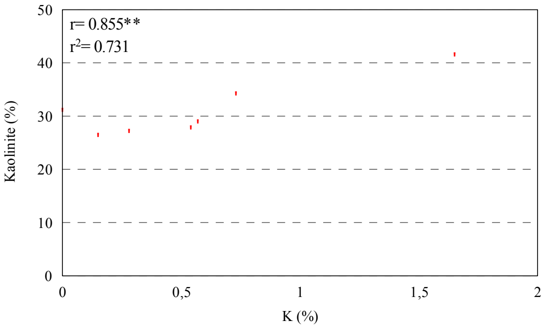


Figure L.3: Ca vs. Mixed Layer for the Münden 1 Profile

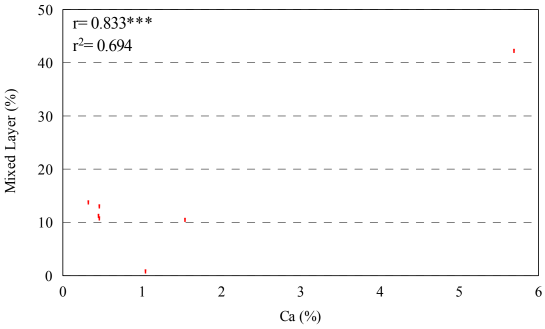
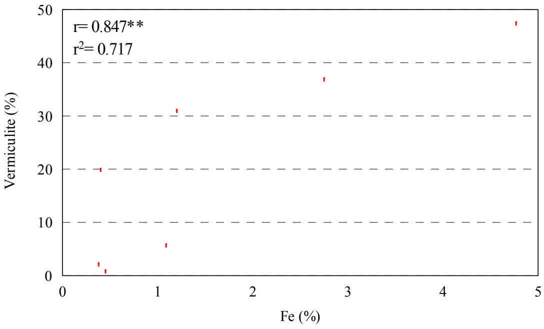
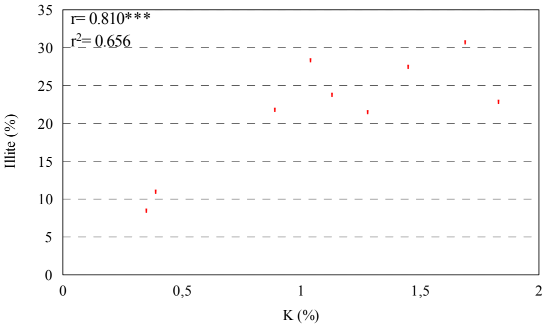


Figure L.4: Fe vs. Vermiculite for the Münden 1 Profile



Profile 2: Münden 2

Figure L.5: K vs. Illite for the Münden 2 Profile



Profile 3: Königstein

Figure L.6: K vs. Illite for the Königstein Profile

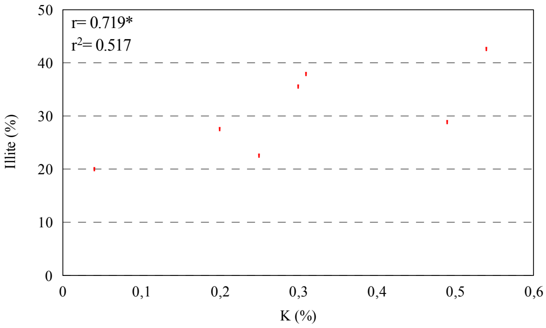
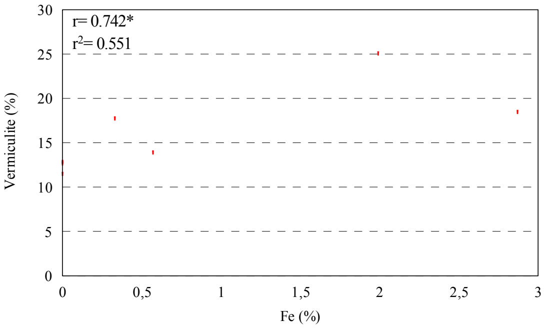


Figure L.7: Fe vs. Vermiculite for the Königstein Profile



Note:
*** Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure L.8: Mn vs. Mixed Layer for the Königstein Profile

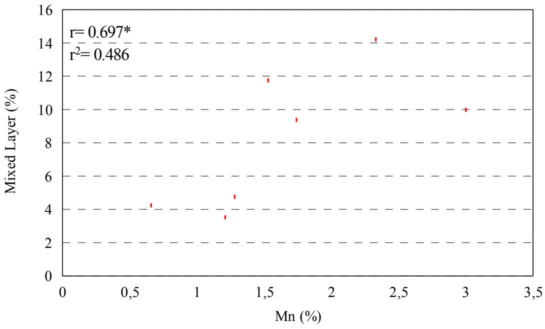


Figure L.9: H vs. Illite for the Königstein Profile

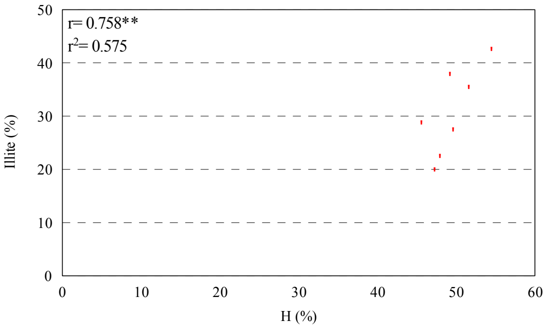
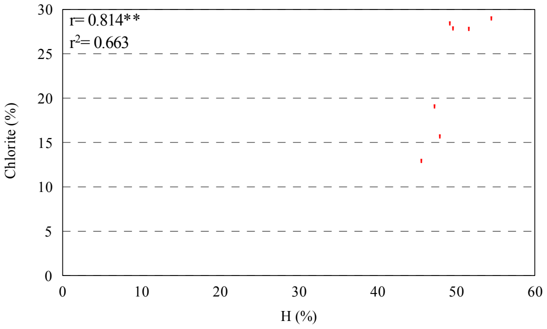


Figure L.10: H vs. Chlorite for the Königstein Profile



Profile 4: Geinsheim

Figure L.11: Na vs. Mixed Layer for the Geinsheim Profile

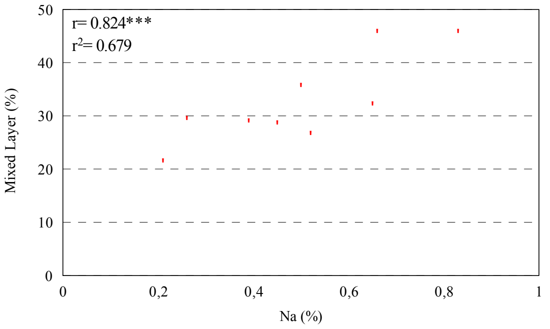


Figure L.12: Na vs. Kaolinite for the Geinsheim Profile

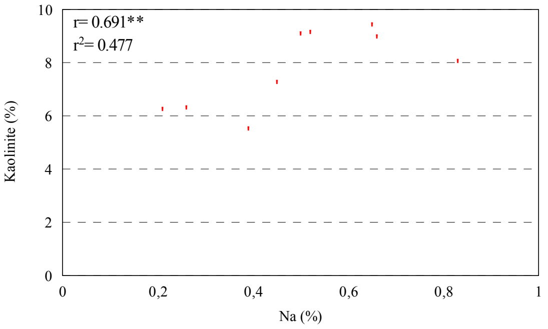
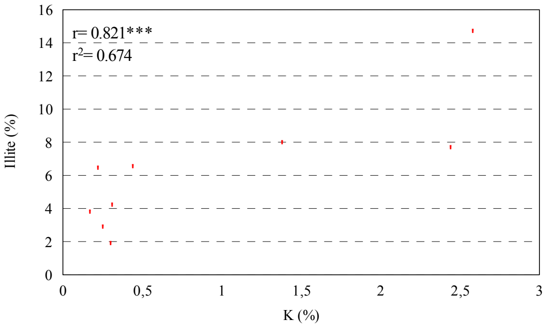


Figure L.13: K vs. Illite for the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Appendix M: Specific Surface Area and the OC and N Contents and C:N Ratios of the Silt and Clay Size Fractions

Profile 1: Münden 1

Figure M.1: OC Content vs. SSA for the Münden 1 Profile

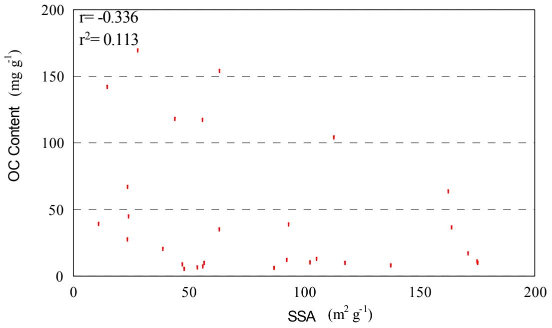


Figure M.2: N Content vs. SSA for the Münden 1 Profile

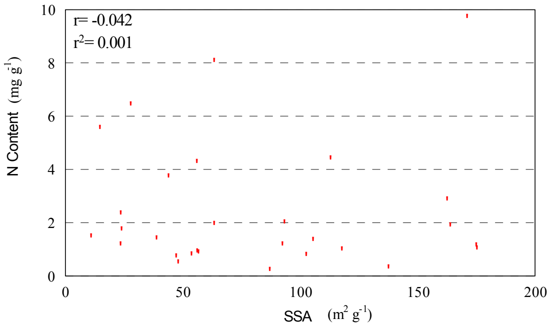
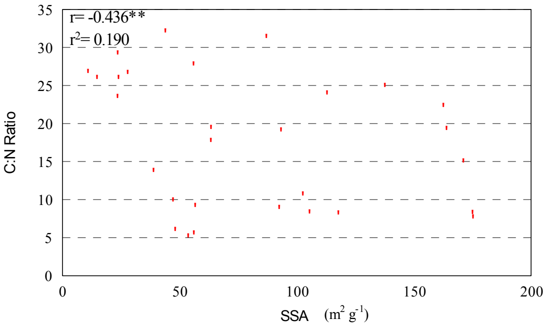


Figure M.3: C:N Ratio vs. SSA for the Münden 1 Profile



Profile 2: Münden 2

Figure M.4: OC Content vs. SSA for the Münden 2 Profile

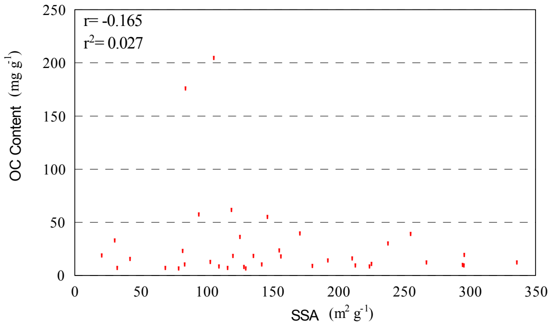


Figure M.5: N Content vs. SSA for the Münden 2 Profile

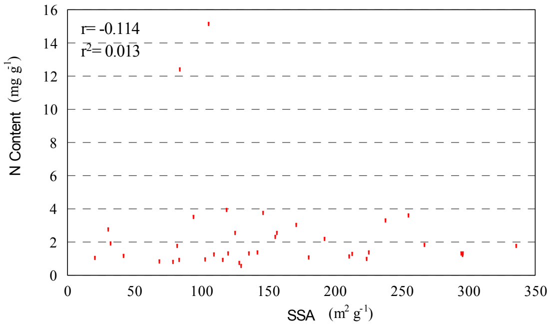
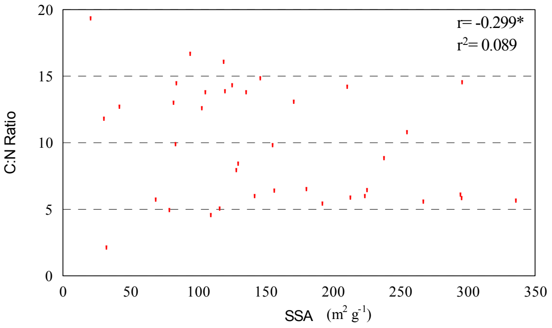


Figure M.6: C:N Ratio vs. SSA for the Münden 2 Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 3: Königstein

Figure M.7: OC Content vs. SSA for the Königstein Profile

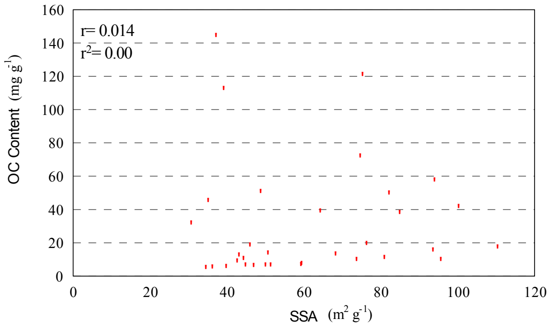


Figure M.8: N Content vs. SSA for the Königstein Profile

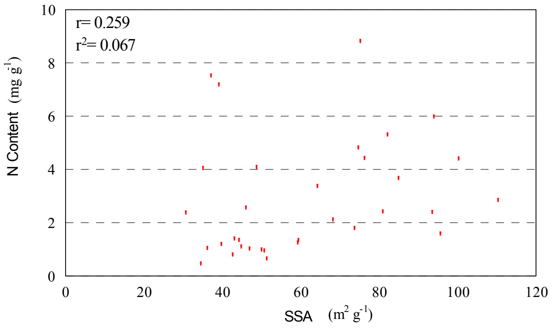
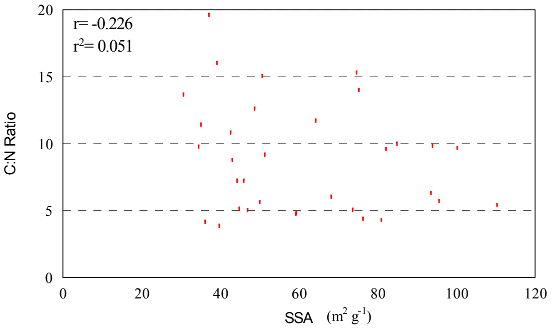


Figure M.9: C:N Ratio vs. SSA for the Königstein Profile



Profile 4: Geinsheim

Figure M.10: OC Content vs. SSA for the Geinsheim Profile

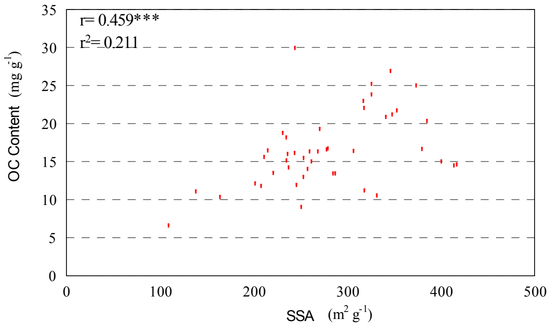


Figure M.11: N Content vs. SSA for the Geinsheim Profile

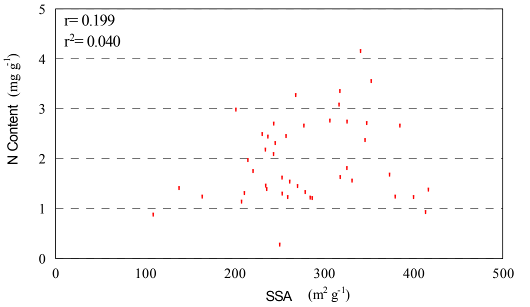
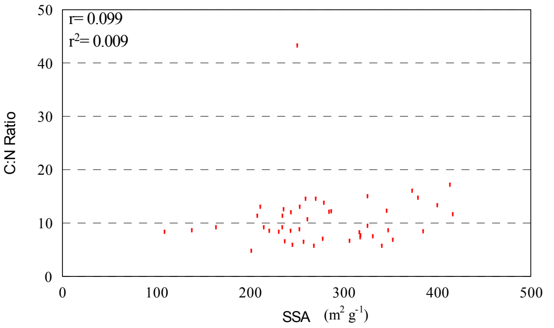


Figure M.12: C:N Ratio vs. SSA for the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 5: Frankfurter Stadtwald

Figure M.13: OC Content vs. SSA for the Frankfurter Stadtwald Profile

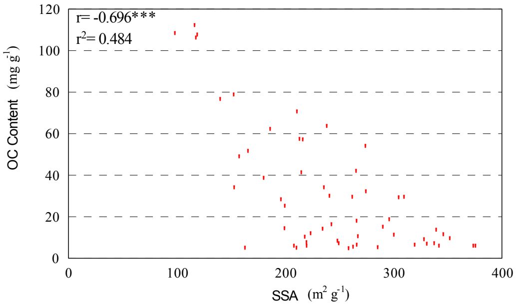


Figure M.14: N Content vs. SSA for the Frankfurter Stadtwald Profile

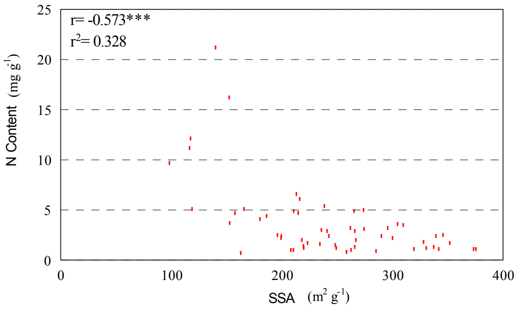
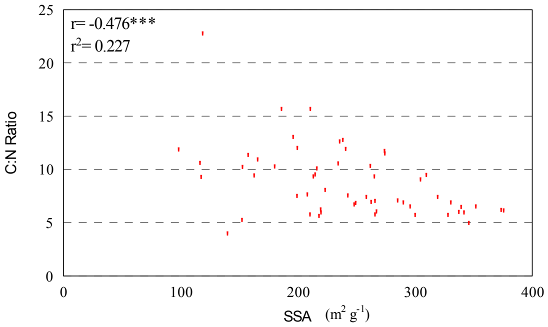


Figure M.15: C:N Ratio vs. SSA for the Frankfurter Stadtwald Profile

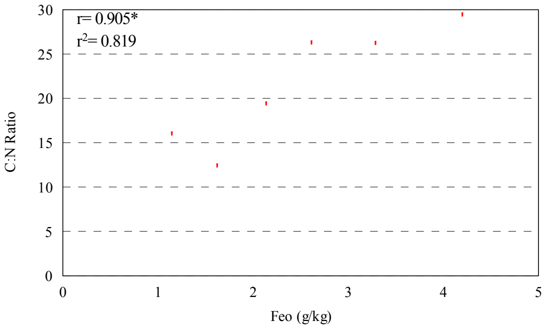


Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Appendix N: Dithionite- and Oxalate-Extractable Fe, Al, Mn and the OC and N Contents and C:N Ratios of Bulk Samples

Profile 1: Münden 1

Figure N.1: Feo vs. C:N Ratio of Bulk Top- and Subsoil Samples (<2 mm) from the Münden 1 Profile



Profile 2: Münden 2

No significant positive statistical correlations were observed for the bulk top- and subsoil samples of this profile.

Profile 3: Königstein

Figure N.2: Feo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Königstein Profile

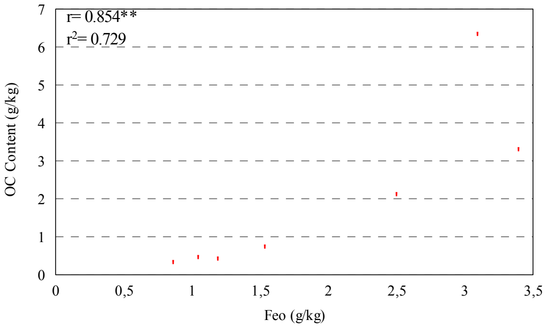


Figure N.3: Feo vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Königstein Profile

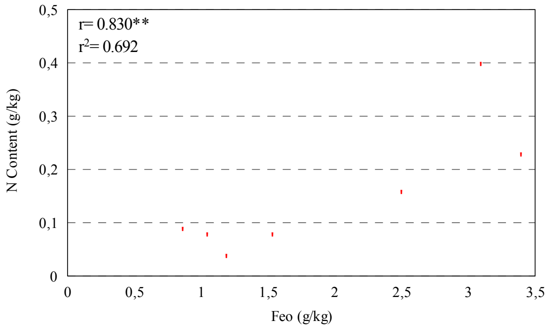


Figure N.4: Feo vs. C:N Ratio of Bulk Top- and Subsoil Samples (<2 mm) from the Königstein Profile

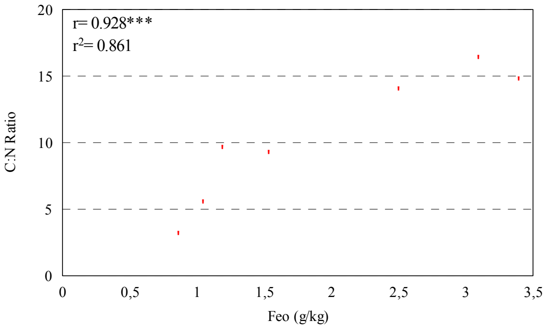
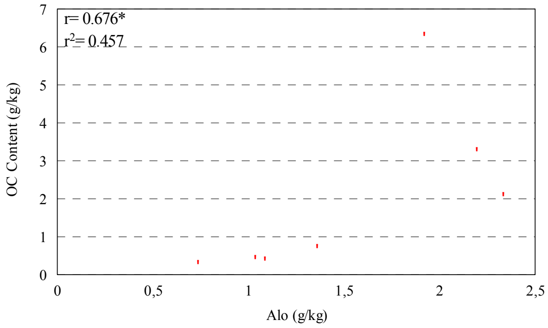
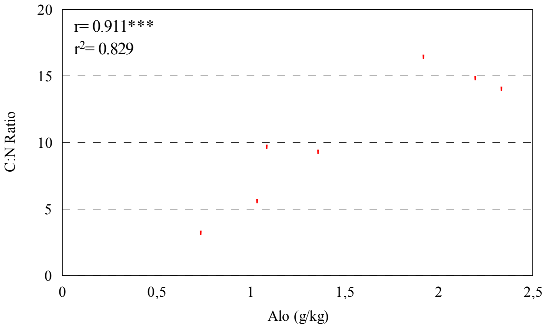


Figure N.5: Alo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Königstein Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure N.6: Alo vs. C:N Ratio of Bulk Top- and Subsoil Samples (<2 mm) from the Königstein Profile



Profile 4: Geinsheim

Figure N.7: Fed vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile

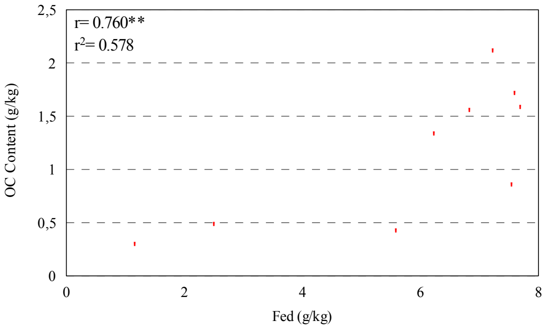


Figure N.8: Fed vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile

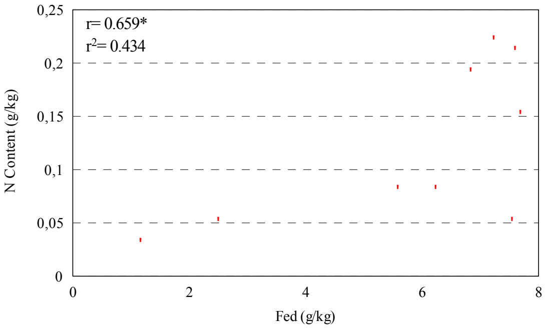


Figure N.9: Feo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile

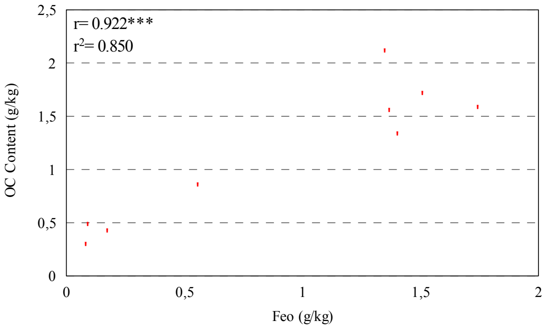


Figure N.10: Feo vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile

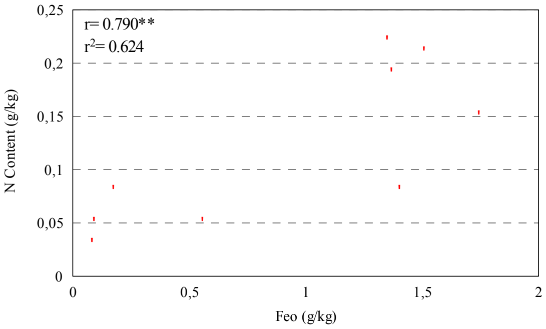


Figure N.11: Alo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile

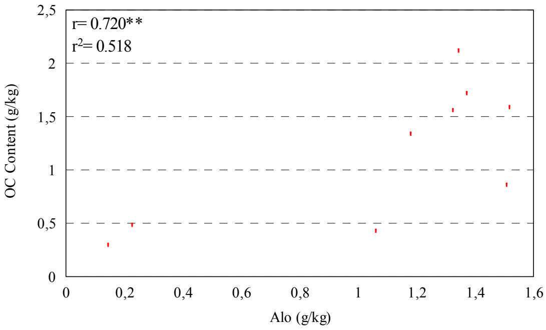
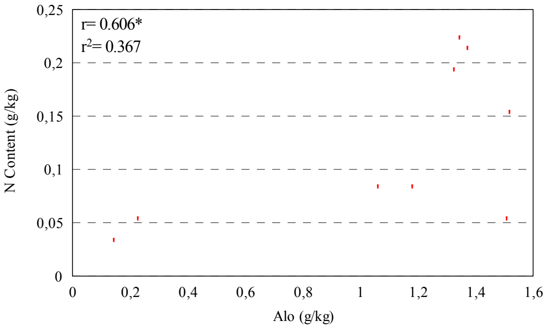


Figure N.12: Alo vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 5: Frankfurter Stadtwald

Figure N.13: Feo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile

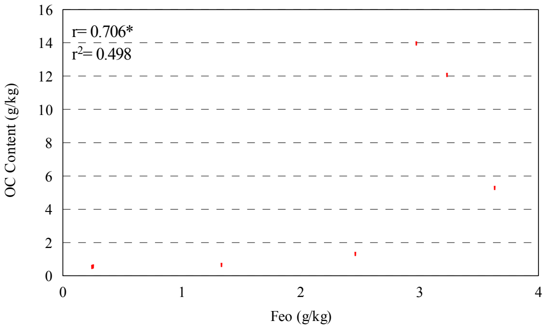


Figure N.14: Feo vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile

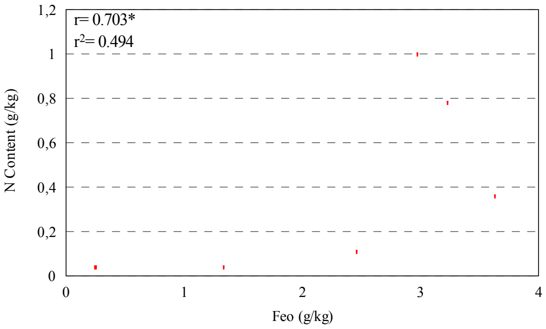


Figure N.15: Alo vs. OC Content of Bulk Top- and Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile

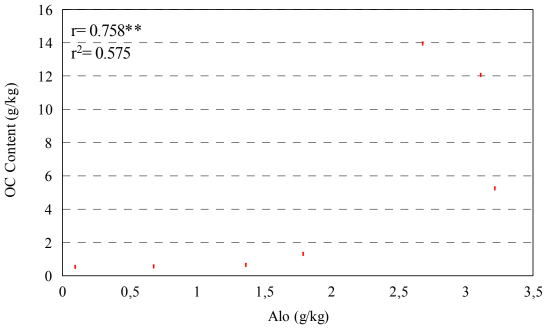
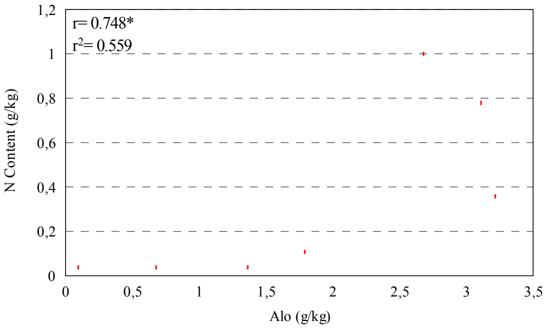


Figure N.16: Alo vs. N Content of Bulk Top- and Subsoil Samples (<2 mm) from the Frankfurter Stadtwald Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Appendix O: Dithionite- and Oxalate-Extractable Fe, Al, Mn and Clay Mineral Composition

Profile 1: Münden 1

Figure O.1: Vermiculite vs. Feo Content of Top- and Subsoil Samples from the Münden 1 Profile

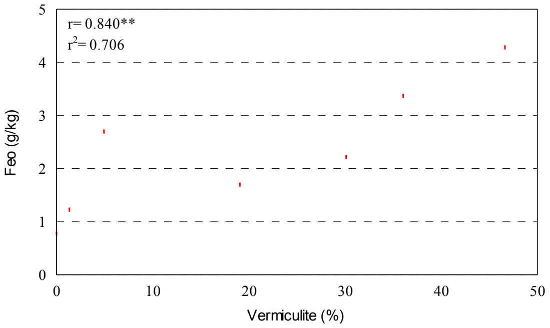


Figure O.2: Mixed Layer vs. Mno Content of Top- and Subsoil Samples from the Münden 1 Profile

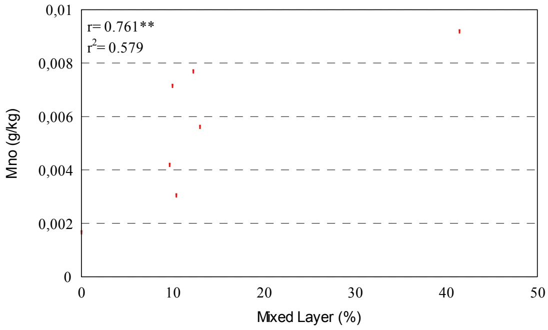


Figure O.3: Illite vs. Fed Content of Top- and Subsoil Samples from the Münden 1 Profile

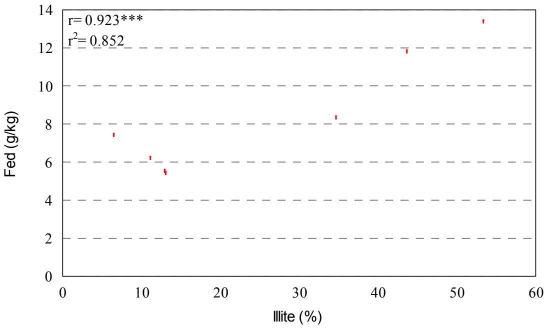
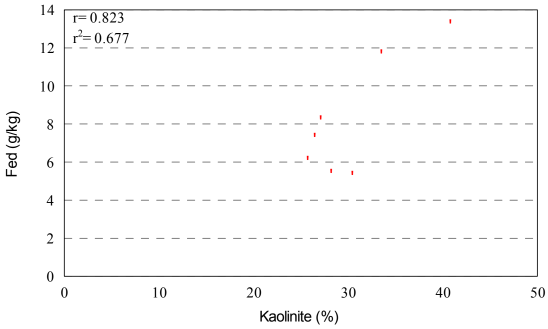


Figure O.4: Kaolinite vs. Fed Content of Top- and Subsoil Samples from the Münden 1 Profile



Profile 2: Münden 2

Figure O.5: Illite vs. Fed Content of Top- and Subsoil Samples from the Münden 2 Profile

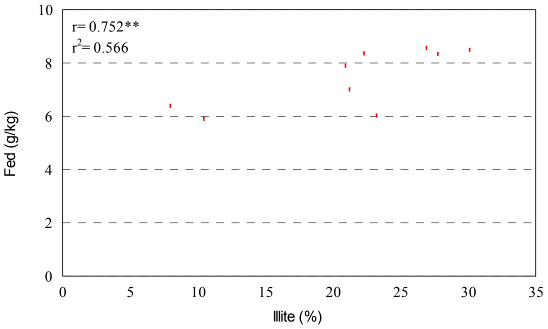


Figure O.6: Illite vs. Mno Content of Top- and Subsoil Samples from the Münden 2 Profile

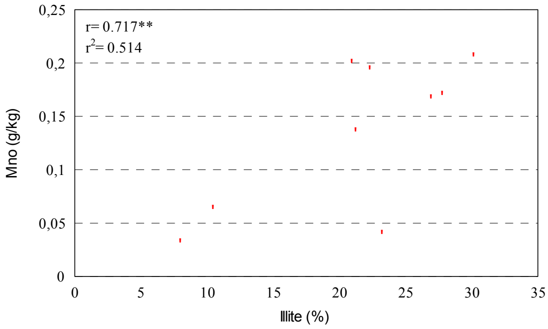
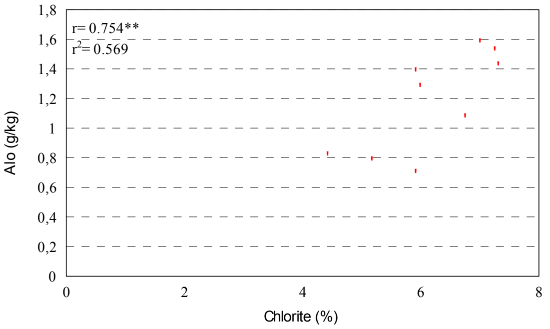


Figure O.7: Chlorite vs. Alo Content of Top- and Subsoil Samples from the Münden 2 Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 3: Königstein

Figure O.8: Vermiculite vs. Feo Content of Top- and Subsoil Samples from the Königstein Profile

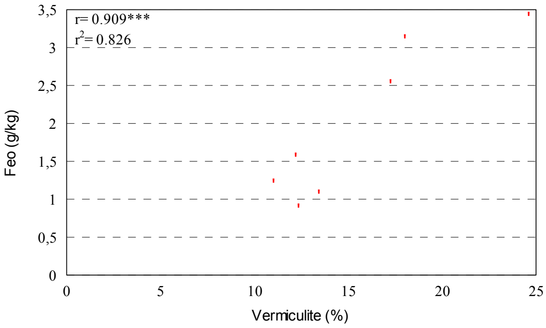


Figure O.9: Vermiculite vs. Alo Content of Top- and Subsoil Samples from the Königstein Profile

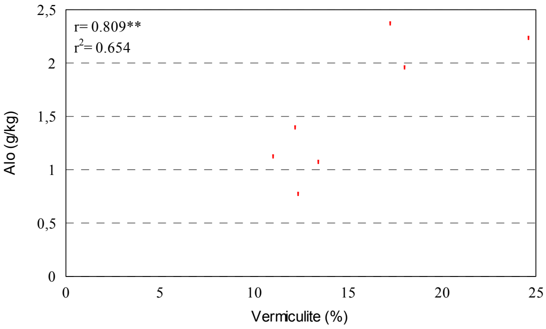


Figure O.10: Kaolinite vs. Feo Content of Top- and Subsoil Samples from the Königstein Profile

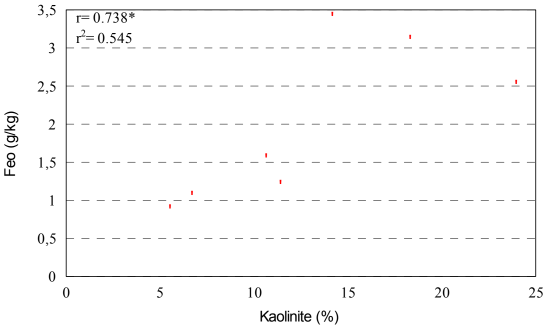
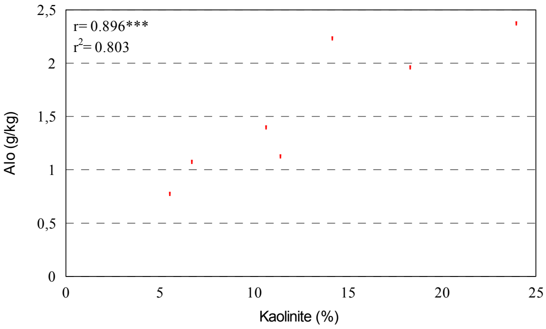


Figure O.11: Kaolinite vs. Alo Content of Top- and Subsoil Samples from the Königstein Profile



Profile 4: Geinsheim

Figure O.12: Mixed Layer vs. Feo Content of Top- and Subsoil Samples from the Geinsheim Profile

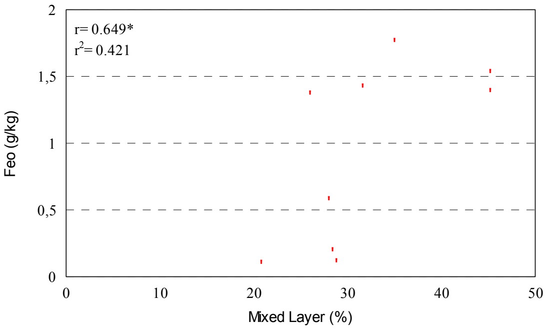
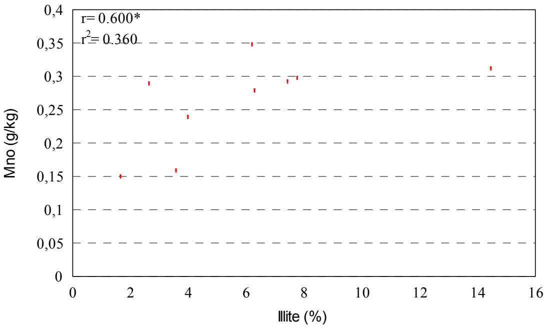


Figure O.13: Illite vs. Mno Content of Top- and Subsoil Samples from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Figure O.14: Kaolinite vs. Fed Content of Top- and Subsoil Samples from the Geinsheim Profile

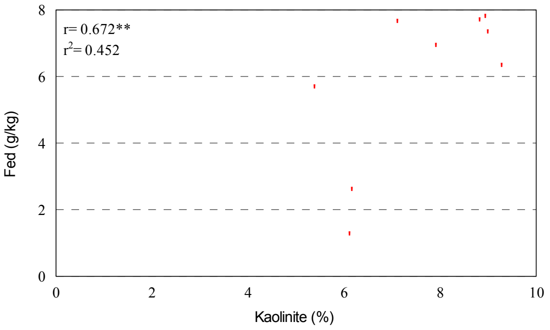


Figure O.15: Kaolinite vs. Feo Content of Top- and Subsoil Samples from the Geinsheim Profile

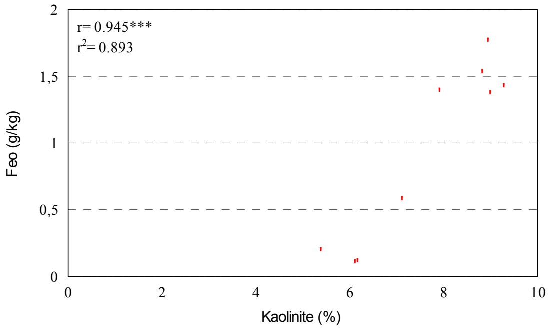
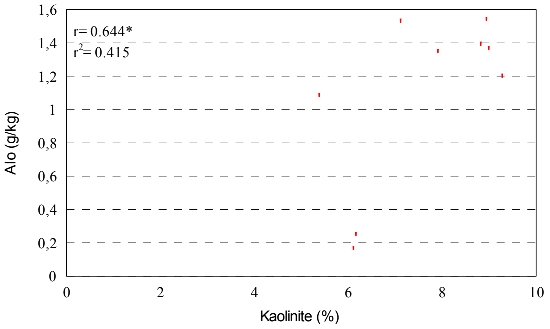


Figure O.16: Kaolinite vs. Alo Content of Top- and Subsoil Samples from the Geinsheim Profile



Note:
***Correlation is at a level of 0.01 significant, **Correlation is at a level of 0.05 significant, *Correlation is at a level of 0.10 significant

Profile 5: Frankfurter Stadtwald

No significant positive statistical correlations were observed for the top- and subsoil samples of this profile.

Cirriculum Vitae

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September 1994 - September 1997	Graduate-Studium: Umweltwissenschaften und Ressourcenmanagement an der Simon Fraser University (British Columbia, Kanada) *Master-Arbeit: „A Risk Balance Analysis of Dioxin and Furan Related Shellfish Closures for Aboriginal Coastal Communities of British Columbia"* **Abschluss: Master of Natural Resources Management** **Prädikat: sehr gut - A (GPA: 3.73/4.00)**

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- Simon Fraser University Graduate Fellowships

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September 1995 - April 1996	**Wissenschaftliche Assistentin** School of Environment and Resource Management, Simon Fraser University (British Columbia, Kanada)
November 1997 – März 1999	**Umweltberaterin** Selbständig

Juni 1999 – September 2002	**Wissenschaftliche Mitarbeiterin** Institut für Mineralogie-Umweltanalytik, Johann Wolfgang Goethe-Universität Frankfurt, Frankfurt am Main, B.R.D.

Publikationen

1. Wiseman, C. und F.A.P.C. Gobas (2002). Balancing Risks in the Management of Contaminated Aboriginal Fisheries. *Int. J. Environ. Heath Res.*: 12 (4): 331-342.
2. Zereini, F., C. Wiseman, J. M. Beyer, S. Artelt and H. Urban (2001). The Occurrence of Platinum, Lead and Cerium in Street Particulate Matter in Frankfurt am Main, BRD. *J. Soils Sed.*: 1(1): 44-49.
3. Zereini, F., C. Wiseman, F. Alt, J. Messerschmidt, J. Müller and H. Urban (2001). Platinum and Rhodium Concentrations in Airborne Particulate Matter in Germany from 1988 to 1998. *Environ. Sci. Technol.* 35: 1996-2000.

Zusätzliche Qualifikationen

- Workplace Hazardous Materials Information Systems (Staatliche Genehmigung zum Umgang mit Gefahrengut)
- Alberta Hunter Education and Conservation Certificate
- Umfangreiche Erfahrung im Umgang mit Computersoftware (z.B. Microsoft Word, Excel, SPSS, Crystal Ball (Monte Carlo Simulation), Powerpoint)
- Sprachen: Englisch (Muttersprache), Deutsch (Fließend)