Analysis of Possible Sources and Pathways of Methyl *tertiary*-Butyl Ether (MTBE) in the Aquatic Environment

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Für meine Mutter

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ZUSAMMENFASSUNG (SUMMARY)

In der vorliegenden Arbeit wurden mögliche Eintragsquellen und Transportwege der Substanz 2-Methoxy-2-methylpropan (Methyl-*tertiär*-butylether, MTBE) in der aquatischen Umwelt in Deutschland untersucht. Die Fragestellungen ergaben sich aus Ergebnissen der Dissertation von Achten (2002), in der ein Überblick über die MTBE Situation in Deutschland erarbeitet und Emissionsquellen ermittelt wurden. Die vorliegende Fortführung dieser Studien sollte einerseits bestehende Langzeitbeobachtungen weiterführen, andererseits den Überblick über die MTBE Situation in Deutschland vervollständigen, indem Proben aus Bereichen der aquatischen Umwelt analysiert wurden, die in der vorangegangenen Arbeit noch nicht oder nur begrenzt berücksichtigt wurden. Zusätzlich wurde das Vorkommen von MTBE in Trinkwassernetzen in Deutschland untersucht.

Die **Jahresproduktion** von MTBE beträgt weltweit ca. 20 Millionen Tonnen (Mio t). Die größten Konsumenten sind die USA mit 61% und Westeuropa mit 12%. Die hauptsächliche **Verwendung von MTBE** ist der Zusatz zu Vergaserkraftstoffen, innerhalb der EU z.B. 98,5% (MEF, 2001). Dies geschieht aus zwei Gründen. MTBE fungiert als Oxygenat, d.h. als organische Verbindung die Sauerstoffatome enthält. Solche Stoffe, meist Alkohole oder Ether, werden Kraftstoffen zugesetzt, um deren Verbrennung im Motorraum zu optimieren, d.h. mit dem Ziel, den Ausstoß von Kohlenmonoxid (CO) und anderen Schadstoffen beim Betrieb der Fahrzeuge zu verringern. Der Zusatz von Oxygenaten erhöht außerdem die Oktanzahl des Kraftstoffes und deshalb werden sie dem Kraftstoff auch als Ersatzstoffe für organische Bleiverbindungen und aromatische Kohlenwasserstoffe zugesetzt. Das weltweit wichtigste Oxygenat stellt MTBE dar, da es sehr gute Additiveigenschaften aufweist und meist schon in den Raffinerien synthetisiert und dem Benzin zugesetzt werden kann. Eine wichtige Rolle als Oxygenat spielt auch Ethanol; in den USA wurden z.B. 2003 8,4 Mio t Ethanol zur Verwendung als Benzinzusatz produziert (RFA, 2004). Geringere Verwendung finden die Oxygenate *tertiär*-Amyl-methylether (TAME), Diisopropylether (DIPE), Ethyl-*tertiär*-butylether (ETBE), Methanol und *tertiär*-Butanol (TBA). MTBE wird in den USA seit Ende der 70er Jahre und in Deutschland seit 1985 als Kraftstoffzusatz verwendet. Der MTBE Verbrauch stieg zu Beginn der 90er Jahre verstärkt an, da 1992 und 1995 die U.S. amerikanischen Gesetze zur Luftreinhaltung (Clean Air Act Amendments, CAAAs) mit der Einführung der Oxyfuel und Reformulated Gasoline (RFG) Programme wirksam wurden. In Regionen, in denen vor allem im Winter die zulässige CO Konzentration in der Luft überschritten wurde, wurde in dieser Jahreszeit die

Verwendung von Oxyfuel mit einem Anteil von 2,7 Gew.-% Sauerstoff vorgeschrieben (1992). In Regionen, in denen zu hohe Ozonkonzentrationen auftraten, wurde der Gebrauch von RFG mit 2 Gew.-% Sauerstoff vorgeschrieben (1995). Um die genannten Sauerstoffkonzentrationen in den Kraftstoffen zu erzielen, müssen 15 Vol.-% bzw. 11 Vol.-% MTBE zugesetzt werden. 1999 betrug der MTBE Verbrauch in den USA 12,7 Mio t (Lidderdale, 2003). In Europa beträgt der Verbrauch von MTBE zur Zeit etwa 3 Mio t und entspricht damit ungefähr der Produktionskapazität (EFOA, 2004a). In den Ländern der EU wird MTBE in unterschiedlichen Anteilen hauptsächlich zur Erhöhung der Oktanzahl den Kraftstoffen zugesetzt. In dieser Funktion ersetzt es die organischen Bleiverbindungen und in zunehmendem Maß auch die aromatischen Verbindungen, v.a. das cancerogene Benzol. Der Anstieg des Verbrauchs von MTBE um 23% zwischen 1995 und 1999 (MEF, 2001) hängt mit verschiedenen EU Direktiven zur Regelung von Kraftstoffmischungen zusammen. Als wichtigste ist dabei die Direktive 98/70/EG zu nennen, die den Gehalt an aromatischen Verbindungen ab dem Jahr 2000 mit 42 Vol.-% und ab dem Jahr 2005 mit 35 Vol.-% begrenzt. Diese Direktive begrenzt gleichzeitig auch den Gehalt an MTBE in europäischen Kraftstoffen auf 15 Vol.-%. In Deutschland wurden im Jahre 2001 etwa 683.900 t MTBE in Vergaserkraftstoffen verwendet. Die MTBE Gehalte in den einzelnen Benzinsorten schwankten im gleichen Jahr zwischen 0,43 Vol.-% (Normal), 3,0 Vol.-% (Super) und 10,2 Vol.-% (Super Plus) (Sur *et al.*, 2003). Die Produktionskapazität beträgt in Deutschland zur Zeit etwa 535,000 t (Pahlke *et al.*, 2000; EFOA, 2004a).

Der Nachweis von MTBE in der aquatischen Umwelt, vor allem in Trinkwasserresourcen, führte in den USA und in Europa zu einer zunehmenden Diskussion über die weitere Verwendung als Kraftstoffzusatz. Das bekannteste Beispiel einer **Trinkwasserverunreinigung** durch einen MTBE Schadensfall trat in Santa Monica, Kalifornien auf, wo im Jahre 1996 etwa die Hälfte der städtischen Trinkwasserversorgung, bedingt durch MTBE Gehalte bis zu 600 µg/l im Grundwasser, geschlossen werden musste. Landesweite Untersuchungen in den USA ergaben, dass MTBE zusammen mit den schon früher verwendeten chlorierten Kohlenwasserstoffen die am häufigsten nachgewiesene leichtflüchtige organische Verbindung (volatile organic compound, VOC) im Grundwasser war (Moran *et al.*, 2004). Dies führte zu den zum Teil schon heute (Kalifornien, Conneticut, New York) wirksamen MTBE Verboten in verschiedenen Bundesstaaten der USA. Als Ersatzstoff bietet sich Ethanol an.

Auch in Europa wurden inzwischen MTBE Kontaminationen des Grundwassers an verschiedenen Standorten entdeckt. Für MTBE liegt bisher keine Legaleinstufung nach europäischem Gefahrstoffrecht vor. In der vom finnischen Umweltministerium im Rahmen der europäischen Altstoffbewertung erstellten Risikoanalyse wurden vor allem (unterirdische)

Tankleckagen als bedenklich hinsichtlich einer Gefährdung des Grundwassers aufgeführt. Bestimmte Risikobegrenzungsmaßnahmen zum Emissionsschutz wurden für notwendig erachtet (Sur *et al.*, 2003). Grundsätzlich will man in Europa zunächst dem Beispiel vieler U.S. Bundesstaaten nicht folgen, d.h. MTBE nicht aus den Kraftstoffen entfernen. Als Gründe hierfür werden hauptsächlich der hohe technische Standard von Lager- und Verteilungsanlagen für Kraftstoff, der niedrigere MTBE Gehalt in europäischen Kraftstoffen und das europäische Besteuerungssystem von Kraftstoffen genannt (MEF, 2001; Env.Exp., 2001; Sur *et al.*, 2003). Als einzige Alternative scheint das bereits in Italien, Frankreich und Spanien verwendete ETBE zur Zeit von mehreren Mineralölgesellschaften favorisiert zu werden. Dies geschieht auch unter dem Gesichtspunkt von Steuererleichterungen, da ETBE mit Bioalkohol hergestellt wird. Bis heute sind allerdings alle Umweltaspekte von ETBE und auch von Ethanol noch nicht hinreichend erforscht.

MTBE wird über die Addition von Methanol an Isobuten in Anwesenheit eines sauren Katalysators hergestellt. Der niedrige Siedepunkt (55°C) und der hohe Dampfdruck (330 hPa bei 25°C) weisen MTBE als VOC aus, die sehr leicht aus Kraftstoffen entweichen kann. Gleichzeitig besitzt MTBE eine hohe Wasserlöslichkeit (42 g/l bei 25°C) und verhält sich wie eine gasförmige Verbindung, d.h. die Henry-Konstante ist berechenbar aus Wasserlöslichkeit und Dampfdruck und beträgt $5{,}38 \cdot 10^{-4}\ m^3$ atm/mol bei 20°C bzw. $2{,}72 * 10^{-4}\ m^3$ atm/mol bei 10 ^oC (Fischer *et al.*, 2004). Zusammen mit seinen schlechten Adsorptionseigenschaften an Bodenmatrices und dem weitgehend persistenten Verhalten gegenüber biologischem Abbau sorgen diese Eigenschaften für eine potentiell weitreichende Verbreitung der Substanz in der aquatischen Umwelt. Außerdem komplizieren und verteuern sie die Sanierung von mit MTBE verunreinigtem Wasser. Im Vergleich zu MTBE tritt Benzol, die nächstlöslichste Benzinkomponente, stärker aus der Wasserphase in die Dampfphase über, besitzt eine 27-fach erniedrigte Wasserlöslichkeit und wird im Untergrund besser retardiert und abgebaut. Der Abbau von MTBE in der Atmosphäre geschieht fast ausschließlich durch die Reaktion mit Hydroxylradikalen zu *tertiär*-Butylformiat (TBF). Die Halbwertszeit in der Atmosphäre beträgt 3-6 Tage. Im Wasser ist das Hauptabbauprodukt TBA.

MTBE kann durch punktförmige und diffuse Quellen in die aquatische Umwelt gelangen. Punktuelle Quellen sind vor allem unterirdische Tankleckagen oder undichte Pipelines. Die resultierenden Konzentrationen im verunreinigten Grundwasser können dann im µg/l-mg/l Bereich liegen. MTBE Kontaminationsfahnen sind, abhängig von den hydrogeologischen

Gegebenheiten, meist länger als entsprechende BTEX (Benzol, Toluol, Ethylbenzol, Xylole)-Fahnen. Für die Verunreinigung von Oberflächengewässern im ng/l-µg/l-Bereich sind MTBE Emissionen über kommunale Abwässer, die meist auch städtischen Oberflächenwasserabfluss (urban runoff) enthalten, sowie Einleitungen MTBE-haltiger industrieller Abwässer als Quellen anzusehen (Achten *et al.*, 2002a). Diese können von Raffinerien, MTBE Produktionsanlagen, Tanklagern (MEF, 2001), aber auch von Anlagen stammen, in denen mit MTBE als Lösungsmittel oder Reagens gearbeitet wird. Bisher gibt es für Abwässer keine gesetzlichen Richtlinien bezüglich MTBE. Beim Transport von MTBE oder MTBE-haltigem Kraftstoff über die Wasserwege können Emissionen vor allem beim Be- und Entladen der Schiffe auftreten. In Oberflächengewässern, die zur Ausübung von motorisiertem Wassersport genutzt werden, wird MTBE entweder durch Abgase, die beim Betrieb der Fahrzeuge direkt in das Wasser eingeleitet werden (Gabele *et al.*, 2000), oder durch Tropfverluste beim Betanken in Yachthäfen (An *et al.*, 2002), ebenfalls in Flüsse oder Seen emittiert. Beim Betrieb von Kraftfahrzeugen und beim Betankungsvorgang gelangt MTBE durch seinen hohen Dampfdruck in die Atmosphäre, aus der es durch Niederschlag wieder ausgewaschen wird. Dieser diffuse Eintrag wurde bereits in den USA (Baehr *et al.*, 1999) und in Deutschland (Achten *et al.*, 2001) nachgewiesen und führt zu MTBE Konzentrationen in Grund- und Oberflächengewässern im ng/l-Bereich. Die MTBE Emissionen in die Luft, die bei der Verwendung von Kraftstoff entstehen, werden als die Haupteintragsquelle von MTBE in die Umwelt angesehen. Die in die Atmosphäre emittierte Menge an MTBE wurde für Deutschland im Jahr 1999 auf 2285 t geschätzt (Pahlke *et al.*, 2000). Modell-Berechnungen ergaben, dass sich MTBE bei ca. 10-20°C in der Umwelt hauptsächlich in der Gas (ca. 90%)- und Wasserphase (ca. 10%) verteilt und dass der direkte MTBE Eintrag in Oberflächengewässer die wichtigste Ursache für die resultierenden Umweltkonzentrationen in diesem Kompartiment darstellt (MEF, 2001; Achten *et al.*, 2002c).

Die Toxizität von MTBE ist noch nicht endgültig geklärt. Neben einigen akuten Auswirkungen wie Reizeffekten und zentralnervösen Beeinträchtigungen zeigten sich bei höheren Konzentrationen als 300 ml/m^3 (inhalativ) bzw. 90 mg/kg/d (oral) in Tierversuchen (90 Tage) auch Effekte wie Blutbildveränderungen oder Organgewichtserhöhungen (MAK, 2000). Cancerogene Effekte in Tierversuchen mit Ratten und Mäusen traten bei Konzentrationen von 300 ml/m^3 (inhalativ) bzw. 250 mg/kg/d (oral) auf. Die vorläufigen Einstufungen die aus diesen Tierversuchen resultierten, reichen von „keiner akuten Gesundheitsgefährdung“ (WHO, 1998), „potentiell cancerogen in hohen Dosen“ (U.S. Environmental Protection Agency, USEPA) (Toccalino *et al.*, 2004) bis zu „krebserzeugende Wirkung Kategorie 3B“, d.h. fundierte

Aussagen über ein mögliches Krebsrisiko beim Menschen liegen noch nicht vor (MAK, 2000). Die ökotoxikologischen Grenzwerte liegen für Süß- und Salzwasserorganismen im mg/l-Bereich. Die Grenzwerte für Trinkwasser, z.B. die von der USEPA vorgegebene Empfehlung von 20-40 µg/l, basieren auf den geringen Geruchs- und Geschmacksschwellenwerten (USEPA, 1997), d.h. die Genießbarkeit von Trinkwasser wird bereits bei geringen MTBE Konzentrationen beeinträchtigt.

Die im Rahmen der vorliegenden Arbeit untersuchten Wasserproben wurden in braunen 100 ml Probefläschchen bei pH 2 (HCl) und 4°C aufbewahrt und transportiert. Bei allen **Probenahmen** und Transporten waren Blindproben mit destilliertem Wasser vorhanden, die parallel zu den eigentlichen Proben analysiert wurden, um eventuelle Querkontaminationen zu erfassen. In Wasserproben wird MTBE mit Hilfe der Gaschromatographie (GC), in der Regel auch in Verbindung mit Massenspektrometrie (MS) analysiert. Peaküberlagerungen von MTBE (z.B. mit 2-Methylpentan) wirken sich bei der Verwendung eines Massenspektrometers im full scan Modus im Gegensatz zu einem Flammenionisationsdetektor (FID) nicht negativ auf die Analytik aus. Um MTBE im ng/l-Bereich noch sicher nachweisen und quantifizieren zu können, bedarf es empfindlicher, lösungsmittelfreier Extraktionstechniken wie Purge and Trap (P&T) oder der Festphasenmikroextraktion (solid phase microextraction, SPME) direkt in der Probe oder im Kopfraum (headspace, HS) über der Probe. Die direkte Analyse von Wasserproben im GC (direct aqueous injection, DAI) wurde ebenfalls als adäquate Methode beschrieben (Schmidt *et al.*, 2000). Im Rahmen eines Ringversuchs wurde die Notwendigkeit der Benutzung von internen Standards bei der Analyse von MTBE in Wasserproben hervorgehoben (Schumacher *et al.*, 2003). Die in den hier beschriebenen Studien untersucheten Proben wurden mit Hilfe der Kombination aus HS-SPME und GC/MS analysiert (Tabelle 0-1) (Achten *et al.*, 2001c). Gegenüber der von Achten *et al.* (2001c) entwickelten Methode wurde in der vorliegenden Arbeit die 50m FS-SE-54-CB-5 Kapillarsäule (Chromatographie Service, Langerwehe) mit einer Filmdicke von 5 µm durch eine J&W Scientific DB-624 Kapillarsäule (60 m, 0,32 mm Innendurchmesser) mit einer Filmdicke von 1,8 µm ersetzt. Der Grund dafür war das zu starke Säulenbluten der FS-SE-CB-5 Säule. Desweiteren wurde die Herstellung von Standardlösungen weiter verfeinert, dabei diente die DIN-Norm zur Herstellung von BTEX-Standardlösungen (DIN 38 407) weitgehend als Vorbild, da eine entsprechende Vorschrift für MTBE noch nicht existiert.

HS-SPME	
Faser	75 µm Polydimethylsiloxan/Carboxen
Probenhaltertemperatur	0°C
Magnetischer Rührfisch	3 mm (895-900 U/min)
Probenbehältervolumen	10 ml
Probenvolumen	4 ml
Probentemperatur	35° C (Wasserbad)
Extraktion	Kopfraum
Einstichtiefe der Faser in den Probenbehälter	0,8 cm
Extraktionszeit	30 min
NaCl-Gehalt der Probe	10%
GC	
Gerät	Thermo Quest, Trace GC 2000 Series
Chromatographische Säule	J&W Scientific DB-624 (60 m, 0,32 mm id, 1,8 µm Filmdicke)
Trägergas	Helium 5.0, 70 kPa (constant pressure Modus)
Split-Verhältnis	1:10
Liner (Innendurchmesser)	0,75 mm
Injektortemperatur	260°C
Einstichtiefe der Faser in den Injektor	4 cm
Temperaturprogramm	1 min 50°C, 10°C/min auf 190°C, 20 min
Konditionierungszeit der Faser	10 min
MS	
Gerät	Thermo Quest, Voyager GC/MS
Ionisierungsmodus	EI^+
Temperatur des Interface	250°C
Temperatur der Ionenquelle	220°C
Scan Modus und Bereich	full scan, 40-600 m/z
Interner Standard	d_3MTBE (deuteriertes MTBE)
Software	Xcalibur 1.0

Tabelle 0-1: Analysenparameter für die Bestimmung von MTBE in Wasserproben.

Für die Durchführung einer Extraktion wurden 4 ml einer Wasserprobe bzw. MTBE Standardlösung entnommen und in einen 10 ml Probenbehälter gefüllt, der bereits die für die resultierenden 10 Gew.-% notwendige Menge an NaCl (460 mg) enthielt. Zusätzlich wurden 40 µl einer 10 µg/l d_3MTBE-Lösung (interner Standard) zugegeben. Anschließend wurde das Vial mit einem Dichtring und einer Bördelkappe verschlossen. Nachdem die Faser im Kopfraum der Probe plaziert war (Einstichtiefe 0,8 cm) wurde die Extraktion nach Einschalten des Magnetrührers gestartet. Die Temperatur der Probe während der Extraktion betrug 35°C, während die Faser durch einen Kühlblock auf 0°C gehalten wurde. Nach 35 min Extraktionszeit wurde die Extraktion beendet und die Analyten im Injektor des GC/MS von der Faser desorbiert und analysiert.

Zur Identifizierung von MTBE dienten die Fragmente m/z 73, 57 und 43. Zur Quantifizierung wurden Eichgeraden aus den Flächenverhältnissen der MTBE Signale in den Ionenspuren m/z 73 und m/z 76 (d_3MTBE) erstellt. Die Nachweisgrenze dieser Methode beträgt 10 ng/l (Achten *et al.*, 2001c). Der durchschnittliche Korrelationskoeffizient bei Dreipunktkalibrierungen im Bereich von 20-5000 ng/l lag bei $R^2=0{,}9997$. Sollten Konzentrationen <20 ng/l bestimmt werden, wurden Blindwerte in die Eichkurven integriert. Relative Standardabweichungen von 10% bei Langzeitmessungen (100 ng/l) und 11% bei Kurzzeitmessungen (20 ng/l) wurden von Achten *et al.* (2001c) bestimmt. Die Wiederfindungsraten betrugen 83-118% bei 100 ng/l (Achten *et al.*, 2001c). Die Methode wurde zur weiteren Validierung im Rahmen eines Laborvergleichstests überprüft, wo sie mit Wiederfindungsraten von 89% (74 ng/l) und 104% (256 ng/l) (Schumacher *et al.*, 2003) bzw. mit relativen Standardabweichungen von 12% und 6% hervorragende Ergebnisse lieferte.

Die Empfindlichkeit und Genauigkeit dieser Methode waren die Voraussetzungen zur Durchführung der nachfolgend beschriebenen Untersuchungen, in denen oft Proben analysiert wurden, die MTBE im Bereich zwischen 10 ng/l und 100 ng/l enthielten.

In den Arbeiten von Achten *et al.* (2002b) und Sacher (2002) bzw. Baus *et al.* (2003) werden das Vorkommen von MTBE in Rhein- und Mainuferfiltrat und in durch Uferfiltration produziertem **Trinkwasser**, bzw. die Schwierigkeiten, MTBE durch die gängigen Aufbereitungsprozesse im Wasserwerk aus dem Trinkwasser zu entfernen, beschrieben. Dies führte zu der Frage, inwieweit MTBE in öffentlichen Trinkwassernetzen in Deutschland nachzuweisen ist. Die entsprechenden Proben (n=83) wurden in 50 Städten und Gemeinden aus Wasserhähnen in Gebäuden, die an die öffentliche Wasserversorgung angeschlossen sind, entnommen. MTBE wurde in 40% der Proben in Konzentrationen zwischen 17-712 ng/l detektiert. Diese Werte liegen um den Faktor 100-1000 unterhalb der bekannten Geruchs- und Geschmacksschwellenwerte Die höchsten Konzentrationen konnten im Wasser von zwei Wassernetzen ermittelt werden, in die höchstwahrscheinlich aufbereitetes Grundwasser eingespeist wird, das von einem großen MTBE Schadensfall beeinflusst wird. MTBE konnte in allen Wassernetzen detektiert werden, die - auf Basis der verfügbaren Informationen durch die entsprechenden Wasserversorger - zum Teil durch aufbereitetes Rheinuferfiltrat versorgt werden. Die Konzentrationen in diesen Proben waren kleiner als 100 ng/l und lagen damit in einem Bereich, der die Ergebnisse aus den Uferfiltrat- und Wasserwerksproben (Achten *et al.*, 2002b; Sacher, 2002; Baus *et al.*, 2003) bestätigte. Im öffentlichen Wassernetz von Frankfurt am Main konnte MTBE in einem Zeitraum von ca. 1,5 Jahren in 15 von 16 Proben bestimmt werden, der Median lag bei 37 ng/l. Trotz der niedrigen Konzentrationen, die meist um eine Größenordnung unter den Geruchs- und Geschmacksschwellenwerten lagen, zeigen die Ergebnisse dieser Untersuchung, dass MTBE teilweise in öffentlichem Trinkwasser in detektierbaren Konzentrationen vorhanden ist. Weiterhin zeigen die Ergebnisse, dass stark kontaminiertes Grundwasser die größte Gefahrenquelle darstellt und dass MTBE auch über den Transportweg Fluss-Uferfiltrat-Wasserwerk bis in die Trinkwassernetze gelangt.

Die durchschnittlichen MTBE Gehalte im Oberflächenwasser in Deutschland wurden einerseits mit Hilfe des equilibrium criterion (EQC) Kompartiment Modells und andererseits aus Untersuchungsergebnissen in deutschen Flüssen berechnet. Die Ergebnisse zeigten eine mehr als doppelt so große Konzentration berechnet aus den Untersuchungsdaten (50 ng/l) als die Konzentration, die sich aus den Modellierungen ergab (19 ng/l). Ein Grund dafür war möglicherweise die Existenz von an **Flüssen** lokalisierten, **punktförmigen MTBE Quellen** (Achten *et al.*, 2002c). Diese Quellen sind vor allem an Stellen zu suchen, an denen MTBE in großen Mengen produziert, gelagert und Kraftstoffen zugesetzt wird, bzw. wo Grundwasserkontaminationen in die Flüsse eingetragen werden. Um solche Quellen aufzuspüren, wurden an drei Standorten in Deutschland Wasserproben (n=49) aus Flüssen entnommen, um den Verlauf der MTBE Konzentrationen vor und nach dem Passieren von MTBE Produktionsanlagen (Marl, Lippe), von MTBE Grundwasserkontaminationen (Leuna, Saale) und von Tanklagern/Raffinerien (Karlsruhe, Rhein) zu ermitteln. In der Lippe war der Einfluß von Einleitungen aus dem Industriepark, in den auch die MTBE Produktionsanlage integriert ist, nur sehr schwach zu erkennen. Die Konzentrationen in den entnommenen Proben schwankten meist um den Mittelwert von 274 ng/l. Im Gegensatz dazu waren in der Saale und am Rhein Konzentrationsanstiege von 24 ng/l auf 379 ng/l, bzw. 73 ng/l auf 5 µg/l zu erkennen.

Diese Anstiege erfolgten jeweils zwischen den zwei Probenahmestellen direkt vor und direkt nach der Grundwasserkontamination an der Saale bzw. der Raffinerie/Tanklager am Rhein. Der genaue Weg des MTBE von den genannten Quellen in die Flüsse konnte im Rahmen dieser Arbeit nicht untersucht werden. Die Identifikation solcher Punktquellen bestätigte die Annahme, dass der für die MTBE Gehalte in Oberflächengewässern sensible Parameter „Direkteintrag in Flüsse“ (Achten *et al.*, 2002c) bei den vorangegangenen Modellierungen unterschätzt wurde.

Die Untersuchung von Niederschlagsproben, die von Achten *et al.* (2001c) durchgeführt wurde, ergab detektierbare MTBE Konzentrationen in der kälteren Jahreszeit im Regen bis zu maximal 85 ng/l. Außerdem wurde die Temperaturabhängigkeit der MTBE Konzentrationen im Regen und Auswascheffekte beobachtet. MTBE konnte in 5 Schneeproben aus ländlichen Regionen detektiert werden, wo das Oxygenat ansonsten im Niederschlag nur sehr schwer nachzuweisen war (Achten *et al.*, 2001c). In der vorliegenden Arbeit wurden gezielt **Schneeproben** aus verschiedenen Regionen in Deutschland untersucht um zu klären, ob MTBE sich unabhängig vom Standort (städtisch oder ländlich) nachweisen lässt und ob sich auch bei den MTBE Konzentrationen im Schnee Muster wie Temperaturabhängigkeit und Auswascheffekte beobachten lassen. Zu diesem Zweck wurden 43 Schneeproben an 13 verschiedenen Standorten gesammelt und auf MTBE analysiert. MTBE konnte in 65% der Proben detektiert werden. Die Konzentrationen schwankten zwischen 11 ng/l und 631 ng/l. Grundsätzlich lagen die Konzentrationen oft oberhalb von 100 ng/l und damit deutlich höher als die Konzentrationen im Regenwasser. Die erhöhte Aufnahme von Schadstoffen durch Schnee wurde bereits bei anderen organischen Stoffen beobachtet und zeigt die höhere Effektivität von Schnee, Schadstoffe aus der Atmosphäre auszukämmen. Dies war neben der Bewegung von Luftmassen und dem geringeren photochemischen Abbau von MTBE in der kälteren Jahreszeit auch der Grund dafür, dass sich die MTBE Konzentrationen in Schnee aus städtischen und ländlichen Regionen nicht signifikant voneinander unterschieden. Die Abhängigkeit der MTBE Konzentrationen von der Temperatur und Auswascheffekte konnten anhand der Proben, die an den Messstationen Schauinsland bzw. Taunus-Observatorium (Kleiner Feldberg) genommen wurden, beobachtet werden.

Zur Vervollständigung des Überblicks über die MTBE Situation in Deutschland wurden 170 **Grundwasserproben** analysiert, die von BTEX/Kohlenwasserstoff (KW) Schadensfällen, aus städtischen und industriell beinflussten Gebieten, sowie nicht-städtischen Gebieten stammten. Die Proben bestanden in der Regel aus oberflächennahem Grundwasser. An sechs der sieben untersuchten Standorte mit BTEX/KW Kontaminationen war auch MTBE in Konzentrationen bis zu 42 mg/l nachweisbar. In den nicht-städtischen Grundwassermessstellen wurde MTBE mit einer Häufigkeit von 24% und einem Median von 177 ng/l nachgewiesen. Die maximalen Konzentrationen in diesen Proben lagen im Bereich von 1-2 µg/l und konnten in Proben aus Wasserschutzgebieten nachgewiesen werden. Die Detektionshäufigkeit in städtischen Proben lag bei 63%. Der Median betrug 57 ng/l. Die höchste Konzentration mit 47 µg/l in den städtischen Proben wurde in der Probe aus einer industriell beeinflussten Messstelle bestimmt. Eine genauere Untersuchung im Umfeld dieses Pegels führte zur Endeckung einer MTBE Kontaminationsfahne. Grundsätzlich waren die ermittelten Grundwasserdaten mit bereits veröffentlichten Daten aus Deutschland vergleichbar (Effenberger *et al.*, 2001a; Klinger *et al.*, 2002). Gegenüber den USA wurde -bezogen auf eine Bestimmungsgrenze von 0,2 µg/l- ein erhöhter landesweiter Median von 1,21 µg/l im Vergleich zu 0,67 µg/l (Moran *et al.*, 2004) berechnet. Allerdings muss bei diesem Ergebnis die aus der U.S.-Studie (Moran *et al.*, 2004) übernommene Bestimmungsgrenze berücksichtigt werden: Der in der vorliegenden Arbeit auf der Basis der Nachweisgrenze von 10 ng/L bestimmte landesweite Median ist mit 0.097 µg/l wesentlich geringer.

Die Einflüsse des MTBE Eintrags durch **Niederschlag**, **städtische Kläranlagen** und **industrielle Abläufe** auf die MTBE Gehalte in deutschen Flüssen wurden von Achten *et al.* (2002a) nachgewiesen. Industrielle Abflüsse sind in diesem Fall Abflüsse aus Industrieanlagen, in denen MTBE als Solvens oder Reagens benutzt wird (ca. 1,5% der europäischen Jahresproduktion). In der vorliegenden Arbeit wurden diese Einflüsse auf der Basis der fortgesetzten **Langzeituntersuchungen** von Niederschlag in Frankfurt am Main, dem **Main** in Frankfurt, sowie einer erhöhten Anzahl von Proben aus städtischen Kläranlagen und industriellen Abläufen weitergehend untersucht. Dies umfasste auch die Ermittlung des **quantitativen Einflusses eines Kläranlagenablaufs** auf die MTBE Konzentrationen im Main. MTBE konnte in 60% der monatlich gesammelten Niederschlagsproben (n=89) bei einem Median von 30 ng/l nachgewiesen werden. In den monatlichen Mainproben (n=67) war MTBE nur in zwei Proben nicht nachweisbar, der Median wurde mit 66 ng/l ermittelt. In industriellen Abläufen (n=34) konnten diskontinuierliche Einträge von MTBE-haltigem Abwasser mit Konzentrationen bis zu 28 µg/l in drei Abläufen bestimmt werden. Der Median der übrigen industriellen Abläufe lag bei 49 ng/l. In den Abläufen der zwei untersuchten städtischen Kläranlagen (n=66) lagen die Mediane bei 92 ng/l und 55 ng/l. Der Vergleich der einzelnen Datenreihen mit den Werten aus dem Main bestätigte die Ergebnisse von Achten *et al.* (2002a):

Der Einfluss von atmosphärisch eingetragenem MTBE findet sich nur in Hintergrundkonzentrationen bis zu 30 ng/l wieder. Da dieser Wert auf Messungen im Niederschlag aus dem Ballungsraum Frankfurt am Main beruht, dürfte der Einfluß des atmosphärischen Eintrags mit 30 ng/L wahrscheinlich überschätzt sein. Die Abläufe aus städtischen Kläranlagen, die auch den städtischen Oberflächenabfluss (urban runoff) enthalten und die Abläufe aus vielen Industriebetrieben zeigten MTBE Konzentrationen, die vergleichbar waren mit den Konzentrationen, die im Main gefunden wurden. Dieser Einfluss war an erhöhten Hintergrundkonzentrationen im Main erkennbar. Durch die synchronisierte Probenahme im Bereich eines Kläranlagenablaufs (Ablauf, Mainwasser vor und nach dem Ablauf) konnte bei vier Versuchen eine maximale Konzentrationserhöhung im Mainwasser von 9% durch einen einzelnen Kläranlagenablauf ermittelt werden. Maximale MTBE Konzentrationen im Main von bis zu 1 µg/l, die bei der Langzeituntersuchung von Mainwasser auftraten, waren wahrscheinlich das Resultat von diskontinuierlichen MTBE Einträgen aus Industriebetrieben, die weit von der Probenahmestelle am Fluß entfernt sein können. Dieser diskontinuierliche MTBE Eintrag führt zu „MTBE Wellen“, die von Gerke *et al.* (2003) beschrieben wurden. Der Vergleich von MTBE Konzentrationen im Zu- (n=117) und Ablauf der untersuchten Kläranlagen ergab Eliminierungsraten von MTBE beim Klärprozess in der Größenordnung von 38-50%.

Die Ergebnisse der vorliegenden Arbeit sind ein Beitrag zur Diskussion um die **weitere Verwendung von MTBE als Kraftstoffzusatz**. 18 Jahre nach seiner Einführung gehört die Substanz MTBE zu den am häufigsten detektierten VOCs in der aquatischen Umwelt und ist in den Netzen der öffentlichen Trinkwasserversorgung nachweisbar. MTBE kann aus vielen diffusen und punktuellen Quellen in die aquatische Umwelt emittiert werden und über verschiedene Transportwege bis in das Trinkwasser gelangen. Dies ist einerseits bedingt durch den Einsatz dieser Chemikalie in einem Massenprodukt wie Benzin, andererseits durch die persistenten Eigenschaften des MTBE. In Deutschland oder Europa existiert noch keine Statistik über Schadensfälle mit MTBE, die in der vorliegenden Arbeit direkt im Zusammenhang mit den Grundwasserprobenahmen und indirekt im Zusammenhang mit den Trinkwasserprobenahmen untersucht wurden. Die Frage stellt sich, wieviel solcher Schadensfälle bis jetzt unentdeckt geblieben sind und eventuell eine Bedrohung für Trinkwasserresourcen darstellen.

Trotz der meist geringen Konzentrationen im Trinkwasser sollte die noch nicht vollständig geklärte Toxizität dieses Schadstoffes und seine geringen Geruchs- und Geschmacksschwellenwerte Anlass zu verstärkten Anstrengungen sein, Alternativen zu dieser Substanz zu finden. Andererseits sollte aber in Europa eine zu schnelle Lösung vermieden werden, da die zur Zeit infrage kommenden Substanzen Ethanol und ETBE mit logistischen Problemen behaftet sind (Ethanol) und die Auswirkungen einer flächendeckenden Anwendung auf alle Bereiche der Umwelt noch nicht komplett evaluiert wurden. Die Geschichte der Kraftstoffzusätze Bleitetraethyl, Benzol und MTBE zeigt, dass eine Untersuchung aller umweltrelevanten Aspekte einer Massenchemikalie so weit als möglich durchgeführt werden sollte, bevor diese eingführt wird. Bis eine Alternative eingeführt werden kann, sollten die von der EU empfohlenen Maßnahmen zum Emissionsschutz (Sur *et al.*, 2003) in allen Ländern der EU konsequent umgesetzt werden. Dies sollte vor allem vor dem Hintergrund der ab 2005 durch die EU Direktive 98/70/EG vorgeschriebenen niedrigeren Aromatengehalte im Kraftstoff geschehen, da aufgrund dieser Regelung erhöhte Oxygenat-Gehalte in europäischen Kraftstoffen zu erwarten sind. Desweiteren sollten Untersuchungsprogamme auch auf TBA ausgeweitet werden. Dieses Abbauprodukt weist eine höhere Toxizität auf als MTBE. In Zukunft könnte das MTBE Problem möglicherweise auch in wachsenden Benzinmärkten wie Osteuropa und Asien auftreten.

INTRODUCTION

Methyl *tert*-butyl ether (MTBE) is used worldwide with an amount of about 20 million tons (Mio t). The two largest markets for MTBE are the USA (61%) and Western Europe (12%). MTBE is a High Production Volume Chemical according to the Organisation for Economic Cooperation and Development (OECD). The by far major use of MTBE is its blending into gasoline, either as anti-smog compound or as octane enhancer. As octane enhancer, it has replaced the alkyl lead compounds and increasingly substitutes aromatic compounds. The commercial production of MTBE began in the 1970's.

During the last years it was shown, that the advantages of the use of MTBE, i.e. the reduction of smog and the good economical and blending characteristics, are overshadowed by the widespread occurrence of MTBE in the aquatic environment. The combination of the properties of MTBE (high water solubility, weak adsorption to soil, large persistence to biodegradability), together with its widespread use in gasoline, made MTBE to a compound of concern for drinking water resources (Clawges *et al.*, 2001). The toxicology of MTBE is not yet finally evaluated (MAK, 2000) and its taste and odor threshold in drinking water is only about 15 micrograms per liter (µg/L). The remediation of MTBE contaminated (ground)water is difficult and expensive, due to the persistent behavior of MTBE.

The problems that MTBE can cause were first described in the U.S. during the 1990's (e.g. Squillace *et al.*, 1996). A popular and often cited case of heavy drinking water contamination with MTBE occurred in Santa Monica, California, where half of the drinking water wells had to be closed. There are results from large MTBE surveys carried out in different regions of the U.S. In these surveys, mainly the occurrence of MTBE in drinking water resources was investigated, but also point and non-point sources of MTBE in the aquatic environment were evaluated (Squillace *et al.*, 1996; Moran *et al.*, 2004). MTBE was one of the most detected volatile organic compounds (VOCs) and its detection frequencies were similar to the detection frequencies of some other VOCs (e.g. chlorinated hydrocarbons), that have much longer production and use histories (Moran *et al.*, 2004). Point sources like leaking underground storage tanks (LUSTs) of gasoline can cause MTBE concentrations in groundwater in the µg/L-mg/L range. Non-point sources such as the input of MTBE into surface water and groundwater via atmospheric washout, can lead to MTBE concentrations in the ng/L-µg/L range.

Since the end of the last decade, the oxygenate became subject of discussion also in Europe. The legal aspects of the use of gasoline, the taxation of gasoline, the regulation of emission controls, the regulations of gasoline composition and subsequently the amounts of MTBE used in the different countries in Europe are at least in part significantly different to the single states in the U.S. However, the uncertainties regarding the possible threat created by the distribution of MTBE in the aquatic environment are similar. Some states of the U.S. recently reacted and phased-out MTBE from gasoline. Ethanol is seen as substitute of choice. In Europe, the EU made a risk assessment on MTBE (MEF, 2001), because MTBE belongs to the group of "existing" substances, that require an evaluation of the risks to human health and the environment. The measures of protection that were recommended within the risk assessment will be implied by the single EU member states in different national regulations. Compared to the U.S., there is a lack of MTBE monitoring data from the EU. These data are important first to evaluate the actual occurrence of MTBE, second to develop an understanding of the release and distribution of MTBE in the environment and third, to model the future impacts of a possible increasing use of MTBE during the next years.

The available monitoring data from Europe were summarized within the EU risk assessment report. Investigations on the sources, the occurrence and the disrtibution of MTBE in the aquatic environment in Germany were conducted by Brauch *et al.* (2000), Effenberger *et al.* (2001a), Sacher (2002), Klinger *et al.* (2002), Stockerl (2002), Blankenhorn (2002), Baus *et al.* (2003), Gehrke *et al.* (2003), and Forner *et al.* (2003). The studies conducted by Achten *et al.* were summarized in a dissertation (Achten, 2002). In this dissertation methods were described, how MTBE can be quantitatively detected in gasoline samples (Achten *et al.*, 2001d) and how low MTBE concentrations in environmental water samples in the range of 10-50 ng/L can be determined by using headspace – solid phase microextraction (HS-SPME) and gas chromatography – mass spectrometry (GC/MS) (Achten *et al.*, 2001b). This method was used to analyze environmental water samples from Germany for their MTBE content, mainly precipitation and surface water. In addition, sewage water from municipal sewage plants and industrial plants was investigated. The results of these studies, together with calculations using the equilibrium criterion (EQC) model were used, to get an evaluation of the MTBE situation in the aquatic environment in Germany. The results of the single studies led to new questions. The purpose of the present work was to continue these studies, to clarify some of the questions created by the previous studies and to complete the monitoring data by analyzing groundwater samples, which previously were not included. The objectives of the present study are described in detail as follows:

Analysis of MTBE. The comparability of the results obtained by different methods to determine MTBE in environmental water samples is still subject of discussion (Sur *et al.*, 2003). The method described by Achten *et al.* (2001b) to analyze MTBE at low concentrations in water samples was compared to other methods in the framework of an interlaboratory comparison study and provided excellent results. The method was further improved, in particular the making of standard MTBE calibration solutions was further upgraded.

MTBE in Drinking Water. Achten *et al.* (2002b) and Sacher (2002) described the occurrence of MTBE in riverbank filtered water and drinking water produced by riverbank filtration. In addition, the difficulties to eliminate MTBE during drinking water processing were described by Baus *et al.* (2003). From these results the question arised, if MTBE can be found in detectable amounts in finished drinking water in Germany. Drinking water samples from all over Germany were analyzed within the present study to get an answer to this question. Furthermore the results were compared to additional information on the sources of the drinking water to clearify, if certain drinking water systems are more susceptible to MTBE contaminations due to the origin of the drinking water, e.g. from bank filtrated water or groundwater probably affected by nearby contaminated sites.

MTBE Point Sources. The comparison of calculations using the EQC model and average surface water concentrations of MTBE in Germany revealed a more than twice as high concentration on the basis of the monitoring data than the concentration obtained by the compartment modeling (Achten *et al.*, 2002c). One reason for this discrepancy might be an underestimation of the MTBE input from yet unknown point sources into surface water in Germany. In the present study therefore three sites with possible point source releases of MTBE were investigated by sampling river water at these locations. The spatial distribution of MTBE in the rivers should indicate the presence of such point source releases that may account for the yet underestimated MTBE input into surface water.

MTBE in Snow Samples. The atmospheric pathway of MTBE in Germany was investigated by analyzing precipitation samples from urban and rural locations. Thereby, a temperature dependency, wash-out effects and positive MTBE detections in five snow samples from remote areas were observed (Achten *et al.*, 2001). An objective of the present study was to clearify, if similar observations (temperature dependency, wash-out effects) can be observed in snow samples and if the trend, that MTBE can be detected in snow samples independent of the location (urban or rural) is confirmed on the basis of a larger sample amount.

Groundwater. The investigation of groundwater was not carried out in the studies of Achten (2002) and although there are monitoring data from Germany available, even more data are required (Klinger *et al.*, 2002) to complete the overview on the MTBE situation in Germany. Therefore groundwater samples were collected and analyzed in the present work. The samples originated from gasoline contaminated sites, non-urban sites in water protection areas and urban sites, which are in part industrially influenced.

Long-Term Monitoring. The different influences of precipitation, industrial and municipal sewage plant effluents on the MTBE contents in river water could be demonstrated by Achten *et al.* (2002a). These studies were continued to confirm the findings on the basis of a larger data set, in particular the data set of sewage water samples was enlarged. This investigation also required the continued long-term monitoring of water from the river Main and precipitation in Frankfurt am Main. In addition, the influence of municipal sewage water on the MTBE contents in the river Main was quantitatively investigated.

1. PRODUCTION, USAGE AND LEGAL EMISSION CONTROL OF MTBE

1.1. Production and Usage

1.1.1. USA

The addition of MTBE to gasoline is carried out for two reasons. First, MTBE increases the octane number of the blended gasoline. For this purpose, MTBE has substituted organic lead compounds since the end of the 1970’s in the U.S. and since 1985 in Europe. Commercial production of MTBE for this purpose started in the U.S. in 1979. The second reason for the addition of MTBE to gasoline is its usage as an oxygenate to increase the oxygen content of the blended gasoline. Oxygenates are organic compounds that contain oxygen atoms, i.e. alcohols and ethers. Oxygenate blended gasoline causes less emissions, in particular emissions of carbon monoxide (CO), since the combustion of the leaner mixture in the motor is more complete. In the year 1990, the U.S. Clean Air Act Amendments (CAAAs) were passed, that require since 1992 areas exceeding the national ambient air quality standard for CO (carbon monoxide nonattainment areas) to use gasoline with a minimum oxygen content of 2.7 % w/w (Oxyfuel) during the wintertime, when the CO concentrations are highest. The reformulated gasoline program followed in 1995 and requires metropolitan areas with serious ozone problems to use reformulated gasoline (RFG) with an oxygen content of 2% w/w. These requirements were mainly achieved by blending the gasoline with MTBE, due to its low cost, ease of production and favorable transfer and blending characteristics (Squillace *et al.*, 1996). The requirements of 2.7% and 2% oxygen w/w correspond to MTBE concentrations of 15% w/w and 11% w/w, respectively. MTBE was the 39th highest produced organic chemical in the U.S. in 1970, whereas it has become in 1998 fourth highest, after ethylene, propylene and 1,2-dichloroethane, due to its demand caused by the two gasoline programs (Johnson *et al.*, 2000). Figure 1-1 illustrates the MTBE supply in the U.S. from 1995-2001 and in addition the consumption of ethanol, the second most used gasoline oxygenate in the U.S. The discrepancy line indicates, that during the first years of the RFG program almost all of the consumed MTBE was added to reformulated and oxygenated gasoline. In the following years, MTBE was increasingly added also to conventional gasoline, mainly as an octane enhancer (Lidderdale, 2003). MTBE was imported not only as pure substance, but also in RFG. The reason for this might at least in part be due to the fact, that some refineries in the U.S. are overaged and cannot be used to produce

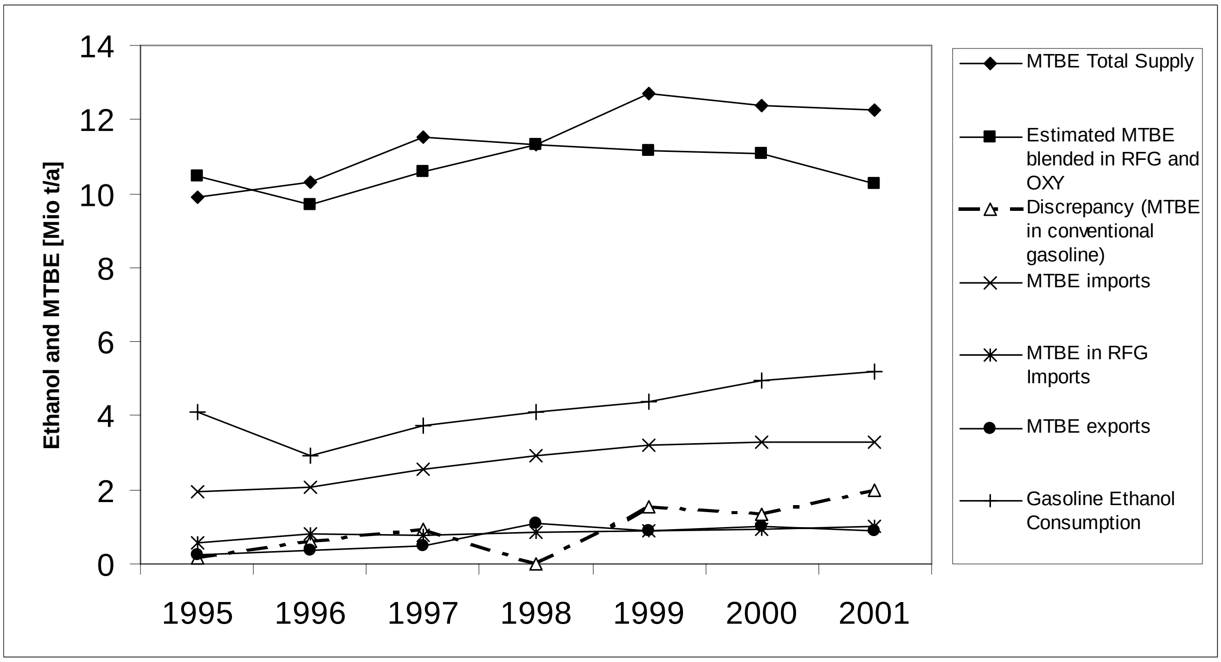

Figure 1-1: MTBE supply in the U.S. from 1995-2001. The discrepancy line indicates MTBE total supply – estimated MTBE consumption in RFG and Oxyfuel (Lidderdale, 2003). In addition the gasoline ethanol consumption is illustrated (Berg, 2004).

gasoline in variable compositions with respect to the different requirements in the areas where the gasoline is sold. Figure 1-1 furthermore shows the constant growing market for gasoline ethanol from 2.9 Mio t (1996) to 5,2 Mio t (2001), whereas the demand for MTBE after the maximum of 12.7 Mio t in the year 1999 slightly declined, which was expected (EFOA, 2004a). The enacted phase-out of MTBE from gasoline in many states of the U.S. will furthermore increase the market share of ethanol, the only substitute that is considered at the moment. The MTBE bans in different states were enacted due to MTBE findings in the aquatic environment and the possible threat for drinking water resources that was derived from these findings. In addition, farmstate lawmakers pushed the MTBE ban. A description of the factors that led to the political measures was already given by Achten (2002). In the year 2003, the production of gasoline ethanol increased to 8.4 Mio t in the U.S. (RFA, 2004). However, only the bans of five states, i.e. California, Conneticut, Kentucky, Missouri, and New York, are forecasted to have a significant direct effect on MTBE and gasoline markets, since they consume about 50% of the MTBE blended into RFG and oxygenated gasoline (Table 1-1). The market share of other oxygenates such as ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), *tert*-butyl alcohol (TBA) and methanol is limited (Squillace *et al.*, 1996; Schmidt *et al.*, 2001a).

State	**MTBE phaseout date**	**MTBE average annual consumption [kt/a] 2001**
MTBE bans enacted:		
California	Jan. 1, 2004	3.43
Conneticut	Oct. 1, 2003	0.4
Kentucky	Jan. 1, 2006	0.09
Missouri	Jul. 1, 2005	0.13
New York	Jan 1, 2004	0.91
No MTBE bans enacted		
Arizona		0.15
Delaware		0.13
Dist. Of Columbia		0.03
Maine		0
Maryland		0.54
Massachusetts		0.72
New Hampshire		0.14
New Jersey		1.17
North Carolina		0
Pennsylvania		0.42
Rhode Island		0.11
Texas		1.31
Utah		0
Virginia		0.58
MTBE bans in Illinois, Colorado, Indiana, Iowa, Kansas, Michigan, Minnesota, Nebraska, Nevada, Ohio, South Dakota, and Washington were also enacted (2000-2005), but these states do not consume MTBE.		

Table 1-1: MTBE bans in different U.S. states. The table does not include MTBE blended into conventional gasoline, e.g. in Maine, that rejected from the RFG program. For further information see Lidderdale et al. (2003).

It is expected, that the ethanol industry is able to meet the demand for ethanol in the states that have banned MTBE. The Renewable Fuels Association (RFA) resumed in its outlook for 2004 regarding the shift of California, Conneticut and New York to ethanol: "By rapidly expanding production capacity, the ethanol industry successfully met the growing needs of these markets and ensured a smooth transition from MTBE to ethanol". However, net changes of –11% to -12.2% in gasoline production capacity of California's refineries due to the California MTBE ban were calculated. The substitution of MTBE with ethanol causes loss of gasoline volume, since two liters of MTBE are substituted by about one liter of ethanol. The pump price and the costs of producing RFG were projected to increase (Lidderdale, 2003) (see also Chapter 2.7.).

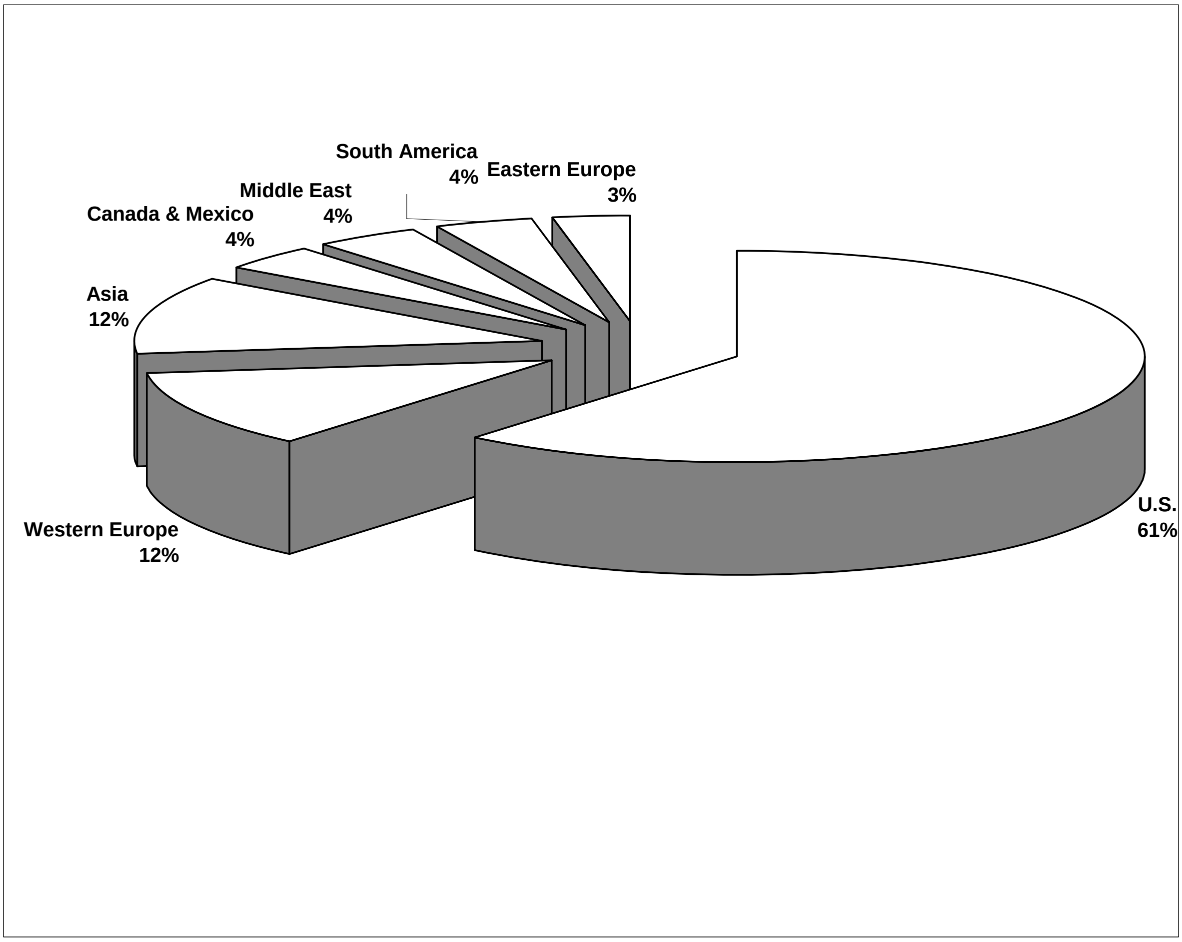

Figure 1-2: Worldwide demand for MTBE in the year 1999 (Thayer, 2000).

Figure 1-2 illustrates the worldwide demand for MTBE in the year 1999 with $26.65*10^9$ L (19.75 Mio t). After the U.S., Asia, Western Europe, Canada and Mexico have the highest demand for MTBE. In Mexico gasoline contains about 5-7.5% v/v MTBE (Schifter *et al.*, 2001). In Canada also ethanol is used widely, similar to Brasil (Achten, 2002). An increase in the MTBE use from 2.3 Mio t in the year 1999 to 5.1 Mio t in the year 2010 is assumed in Asia (De Witt, 1999). The world market of ether oxygenates today can be reasonably estimated by using only MTBE figures, as the volume of TAME and ETBE combined is small compared to MTBE (EFOA, 2002). Since 1992, the MTBE market has been in continuous growth. Between 1992 and 1998 an annual growth of about 12 % could be observed. The 1998 world consumption of 19,5 Mio t/a was about double the consumption in the year 1992. The driving force for the growth were the U.S. Clean Air Act Amendments (CAAAs) (EFOA, 2002). Present trends indicate a mild growth in 2000, up to 20 Mio t, with U.S. consumption slightly declining and other parts of the world growing, e.g. the Asian market. The market growth for the next years is forecasted to be very minor. Forecasting is difficult due to the uncertainties, which may have negative impacts on the world's largest market, i.e. the U.S. consumption (EFOA, 2004).

1.1.2. European Union (EU)

Western Europe, taken as a whole, is the second largest market for motor gasoline in the world. In 1997, the volume consumed in Western Europe was about 40% of the volume consumed in the U.S. (MEF, 2001). Commercial production of MTBE started in Europe in 1973 (Italy). After the introduction of unleaded gasoline in Europe in the 1980's the demand for MTBE as octane enhancer increased and the oil companies started to produce MTBE within the refineries. In addition, the EU directive 85/535/EWG introduced in 1985 and requiring the reduction of crude oil by the use of alternative gasoline components also enhanced the demand for MTBE. At the beginning of 2000, this directive was in part substituted by the EU directive 98/70/EG from 1998, which regulates the quality of gasoline. The directive set new mandatory specifications on gasoline, i.e. that from 2000 and 2005 on, the aromatic content in gasoline is limited to 42% v/v and 35% v/v, respectively. The directive furthermore regulates the legal maximum concentration of "ethers containig five or more carbon atoms per molecule" to 15% v/v. An authorization for the blending of gasoline with alcohols and ethers was not mandatory before the directive 85/535/EWG was introduced (Sur *et al.*, 2003).

Because of these developments, the MTBE consumption in Europe has increased by 23% between the years 1995 to 1999 (MEF, 2001). The demand today is about 3 Mio t and approximately equal to the production capacity (Table 1-2) (EFOA, 2004a). In the last few years Europe was a net exporter of MTBE, either as a straight component or blended into gasoline. Data on the MTBE balance in the EU are available for the year 2000 (EFOA, 2002). In this year, an amount of 2,844,000 t were produced within the EU. About 479,000 t were exported outside the EU and about 129,000 t were imported. The major proportion (>83%) of the exported volume was transported to the U.S. and Canada. 80% of the exported volume were transported as non-blended MTBE and minority as a component of gasoline. Thus, the annual consumption of MTBE within the EU in the year 2000 was 2,495,000 tons (EFOA, 2002). In the year 1997, 6000 t and 29,000 t of MTBE were used as solvent and for the production of isobutylene, respectively. This means, that about 1.5% of the MTBE produced is used for other purposes than its addition to gasoline (MEF, 2001).

Within Europe, the largest amounts of MTBE are produced in The Netherlands (Table 1-2, Figure 1-3), which has to date also the largest production capacity, but in the year 1997, more than half of the MTBE produced in The Netherlands was exported (Figure 1-3). During 1997, most MTBE was used in Italy, Germany and Spain. The used amounts in Italy and Spain indicate, that the data that were used for Figure 1-3 (MEF, 2001) probably also include production and usage of ETBE. The MTBE contents in gasoline differ from 0.2% w/w in Denmark to 8.5% w/w in Finland. Prices for super premium gasoline in Denmark were raised by the authorities in order to reduce the consumption of MTBE (Wolff, 2000). In some countries special grades of gasoline are sold, for example in Finland, where reformulated gasoline requires 2-2.7% oxygen (w/w), which is equivalent to 11-15% MTBE (v/v) (MEF, 2001). In Finland, in Belgium and in Great Britain the oxygenates TAME and next-TAME are also used. About 100,000 t of TAME are used as fuel oxygenate in Finland. In the year 1998, about 160,000 t of ETBE were used in France (Schmidt *et al.*, 2001b), but also MTBE and TAME are used (Achten, 2002). In France, Italy and Spain the consumption of ETBE is expected to increase due to tax incentives for the use of ethanol that is used to produce ETBE (Schmidt et al, 2001b).

Reliable data on the consumption of ETBE in Italy were not available. Sur *et al.* (2003) proposed an amount of 890,000 t, but this number probably is too high considering the production capacity in Italy (Table 1-2). In Spain, the oxygenate production seems to have been converted to ETBE. In the year 2004, the capacities of ETBE producers in Spain and France are 420,000 t/a and 219,000 t/a, respectively (EFOA, 2004a). The production capacity of MTBE in France is still 612,000 t/a, but the produced MTBE seems to be mainly used for export, as suggested by the data from 1997 (Figure 1-3). Table 1-2 indicates, that MTBE can also be produced in reasonable amounts in Eastern Europe. The consumption of MTBE is expected to remain fairly stable in Europe over the next few years (EFOA, 2004a).

Nevertheless, the loss of octane rating in gasoline due to the directive 98/70/EC requires a replacement of about 7-8 Mio t of aromatic compounds by high octane blending gasoline components. MTBE may theoretically be the sole substitue. However, EU legislation does not mandate to oxygenate use and MTBE is a fairly expensive blending component just for octane boost (MEF, 2001). The long range-prospect made by De Witt Co. suggests that MTBE will play the major role in aromatic reduction to meet the 98/70/EC requirements. An amount of about 4 Mio t of MTBE would hence be used per year in the EU until the end of 2005. This demand would be already supplied by the MTBE production capacity in the year 2000 in the EU, especially when exports to the U.S. might tend to decline (MEF, 2001). However, there are also alternatives, e.g. the above mentioned ETBE, which would adress the increase of the proportion of biofuel required by the EU and provide tax incentives. In Sweden, The Netherlands and Italy new ethanol production units were built that allow the MTBE production to be converted to ETBE (Achten, 2002). Some petroleum companies currently are proposing and enhancing the substitution of MTBE by ETBE (Shell, 2003; Stupp, 2004).

Country	**Location**	**Product**	**Capacity [1000 t/a]**	**Country**	**Location**	**Product**	**Capacity [1000 t/a]**
Austria	Schwechat	MTBE	65	Lituania	Mazeikiai	MTBE	80
Belarus	Novopolotsk	MTBE	41	Netherlands	Botlek	MTBE	591
Belgium	Antwerp a	MTBE	183		Europort	MTBE	98
	Antwerp b	MTBE	204		Geleen	MTBE	138
Bulgaria	Bourgas	MTBE	82		Pernis	MTBE	153
Czech Republic	Krapuly	MTBE	92		Rotterdam	MTBE	143
Finland	Naantali	MTBE	110	Poland	Plock	ETBE	120
	Porvoo	MTBE	94	Portugal	Sines	MTBE	50
France	Dunkerkerque	ETBE	65	Romania	Midia	MTBE	35
	Feyzin	ETBE	84		Onesti	MTBE	100
	Gonfreville	ETBE	70		Pitesti	MTBE	40
	Fos sur Mer	MTBE	612		Ploiesti a	MTBE	20
Germany	Cologne	MTBE	31		Ploiesti b	MTBE	25
	Heide	MTBE	12	Serbia	Novi Sad	MTBE	35
	Karlsruhe	MTBE	163	Slovakia	Bratislava	MTBE	52
	Marl	MTBE	214	Spain	Algeciras	ETBE	52
	Wesseling	MTBE	65		Bilbao	ETBE	74
	Leuna	MTBE	50		Huelva	ETBE	50
	Schwedt	ETBE	80		La Coruna	ETBE	52
	Vohburg	ETBE	37		Puertollano	ETBE	67
Greece	Aspropyrgos	MTBE	65		Tarragona a	ETBE	54
	Corinth	MTBE	45		Tarragona b	ETBE	71
Hungary	Szazhalmobatta a	MTBE	55	Sweden	Stennungsund	MTBE	50
	Szazhalombatta b	MTBE	53	Ukraine	Kremenchug	MTBE	24
	Tiszaujvaros	MTBE	31	United Kingdom	Fawley	MTBE	122
Italy	Gela	MTBE	45		Grimsby	MTBE	100
	Milazzo	MTBE	65		Killingsholme	MTBE	82
	Priolo	MTBE	41				
	Ravena	MTBE/ETBE	160*				
	Sannazzaro	MTBE	41				

*Table 1-2: MTBE and ETBE production capacities in Europe 2004 (Pahlke et al., 2000; EFOA, 2004). * Capacity in December 2000 (EFOA, 2004c).*

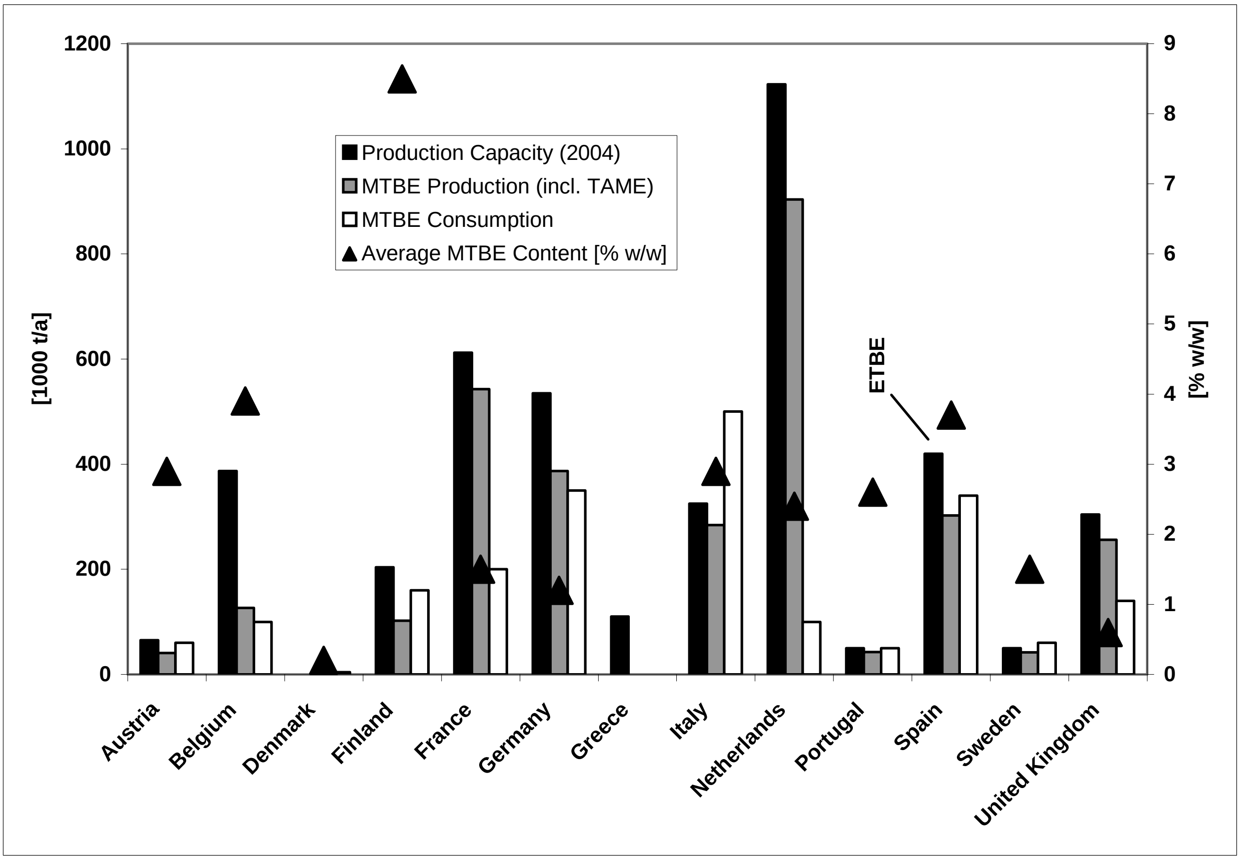

Figure 1-3: MTBE production capacities in the year 2004 (Pahlke et al., 2000; EFOA, 2004a), MTBE production, MTBE consumption and average MTBE contents in gasoline in the year 1997 (MEF, 2001). Note that the production capacitiy in Spain is related to the production of ETBE.

1.1.3. Germany

Since the 1970's, alkyl lead compounds were partly substituted by increased amounts of aromatic compounds, i.e. benzene, toluene, ethylbenzene, xylenes (BTEX) and trimethyl benzenes. The use of catalysts and the phase-out of alkyl lead compounds due to their impact on the environment decreased their use and since 1999, leaded gasoline was not sold anymore. However, the carcinogenic effects of benzene also limited its use and EU legislation required decreasing amounts of aromatic compounds in gasoline (see Chapter 1.1.2.). As a consequence, MTBE has been added to German gasoline since the middle of the 1980's to enhance the octane number of the gasoline. Figure 1-4 illustrates, that MTBE was also blended into super premium leaded gasoline. Since 1992 the consumption of eurosuper increased, accompanied by increasing MTBE amounts blended into this gasoline. The use of regular unleaded gasoline decreased in this period (Figure 1-4 and Figure 1-5). The consumption of MTBE as gasoline additive in Germany reached a maximum of 840,000 t in the year 2000, when also the highest MTBE amounts in the different gasolines were measured (Figures 1-4 and Figure 1-5) (Sur *et al.*, 2003). The highest MTBE concentrations can generally be found in super premium gasoline, but the amounts of this gasoline sold in 2001 were only 11% and 6% of the used amounts of regular and eurosuper, respectively. Nevertheless, super premium gasoline accounts for a 2.8-fold higher amount of MTBE used than regular gasoline. According to Table 1-2, the production capacity of MTBE in the year 2004 is about 535,000 t/a, which is lower than the amount consumed per year in 2000 and 2001. Similar to Europe, an increase in the consumption of MTBE between 1999 and 2005 of about 40-56% was estimated (Achten, 2002). However, there are also efforts in Germany to replace MTBE production by the production of ETBE (Stupp, 2004). The increase of MTBE usage in Germany following the EU directive 98/70/EG was recently estimated to be insignificant due to already low amounts of aromatic compounds in German gasoline (Sur *et al.*, 2003).

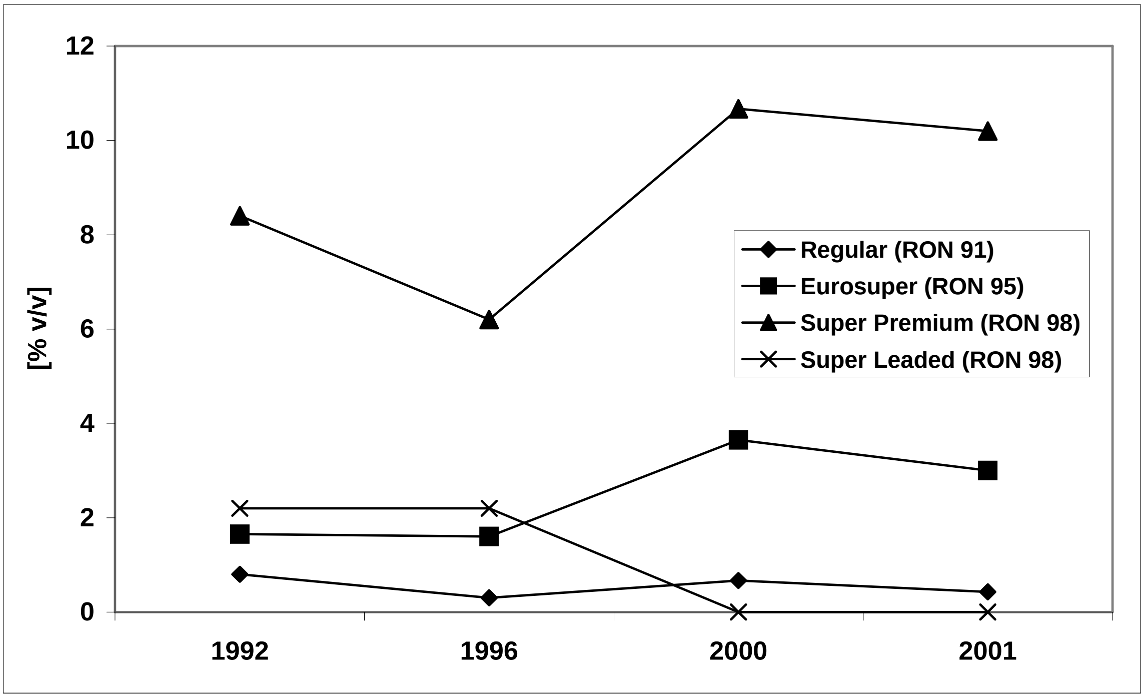

Figure 1-4: MTBE concentrations in different gasolines sold in Germany (RON= research octane number) (Sur et al., 2003).

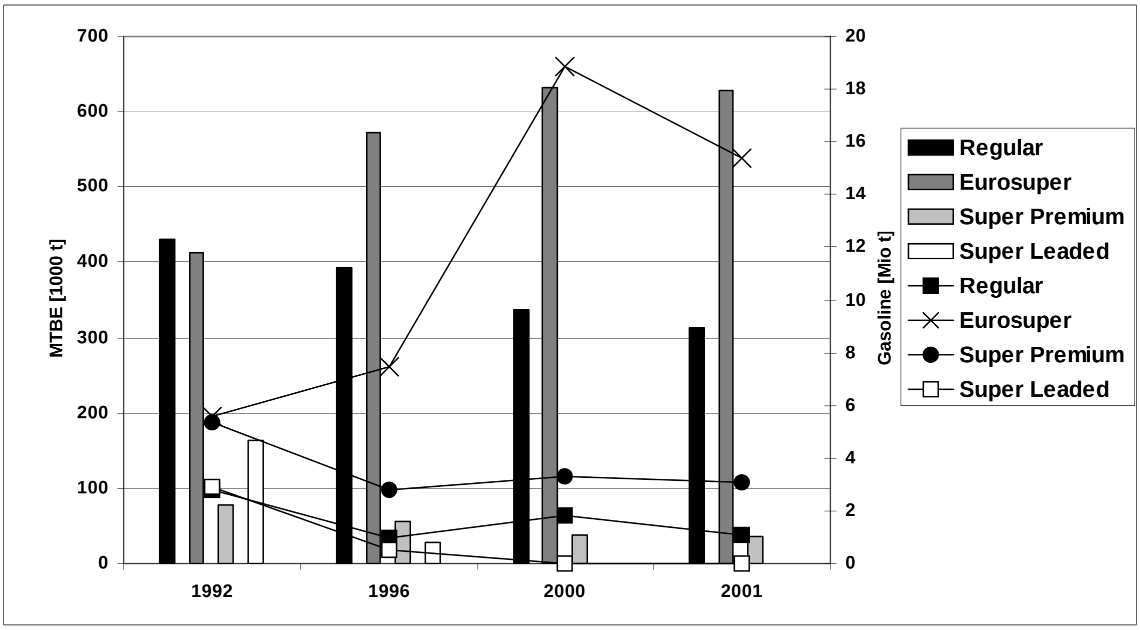

Figure 1-5: Amounts of gasoline consumed in Germany (columns) and consumed MTBE in the different gasolines in Germany (lines) (Sur et al., 2003).

1.2. Legal Emission Control of MTBE

1.2.1. USA

The air reference concentration of MTBE recommended by the USEPA is 3 mg/m^3. This value is related to the daily concentration inhaled that does not represent any risks -except carcinogenic ones- to sensitive humans life-long. The maximum air concentration at working places was recommended at 144 mg/m^3 by the Conference of Governmental Industrial Hygienists. This value is based on a mean working time of 8 hours per day (Achten, 2002).

The detections of MTBE in sources of drinking water and the toxicology of the compound that is not yet finally evaluated led to measures of protection. There was little regulation of underground storage tank (UST) systems in the U.S. before the early1980's. The occurrence of gasoline components in groundwater led to an amendment of the Resource Conservation and Recovery Act (RCRA), that required all UST systems to be installed to certain standards. These standards should achieve to minimize the risk of the contamination of groundwater by leaking gasoline. Existing UST systems were given 10 years to comply from the date the amended act came into force in 1988. Current federal law requires that from the end of 1998, all UST systems must be prevented of corrosion, spill, and overfill protection (Arthur D. Little, 2001). Some states enacted the complete ban of MTBE from gasoline (see Chapter 1.1.1.). The USEPA established a drinking water advisory for MTBE in the range of 20-40 µg/L (USEPA, 1997). These values are based on taste and odor thresholds and they are seen as sufficiently low enough to avoid human health risks. The establishing of a maximum contaminant level for MTBE is expected in the year 2006. The clean-up levels for MTBE mainly in groundwater differ from state to state. These levels range from 10 µg/L in New York to 400 µg/L in Masachusetts. California has established a secondary taste and odor maximum contaminant level of 5 µg/L (Jacobs *et al.*, 2001).

1.2.2. European Union

The possible threat for drinking water sources that is posed by the use of MTBE is generally seen not as high as in some states of the U.S. This point of view is based on different reasons. The already high EU requirements on UST constructions compared to the U.S. are seen as a preventive measure and factor against widespread serious groundwater contamination (Env.Exp., 2001; Sur *et al.*, 2003). In addition, the higher costs of gasoline within the EU compared to the U.S. and the different system of gasoline taxation make it more worth to keep tanks in a good condition (Achten, 2002).

To date, there is no legal classification of MTBE according to the European legislation on hazardous substances. A risk assessment on MTBE was carried out in the framework of European Council Regulation (EEC) 793/93 on the evaluation and control of the risks of "existing" substances by the Ministry of the Environment Finland (MEF, 2001). Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the EU in volumes above 10 t/a. In the framework of this assessment, the following classifications (R-phrases) and security advices (S-phrases) were proposed:

R11:	Highly flammable (F)
R38:	Irritating to skin (Xi)
S2:	Keep out of the reach of children
S9:	Keep container in a well-ventilated place
S16:	Keep away from sources of ignition - No smoking
S24:	Avoid contact with skin

A classification as ecotoxic was not proposed.

As a further result of the risk assessment, measures of protection to prevent risks for groundwater and surface water were proposed. The risk for groundwater was mainly assigned to the impact of MTBE on aesthetic characteristics of groundwater used for the production of drinking water. The consideration of expositions via leaking underground storage tanks (LUSTs) and releases by overfilling tanks was demanded. Measured groundwater concentrations in Europe in many cases were above 15 µg/L, the taste and odor threshold that was considered during the risk assessment. In order to limit the risks for groundwater and drinking water it was recommended that monitoring programs should be established and that the best available techniques should be used during construction or operation of storage/distribution facilities for gasoline. Furthermore the development of EU wide normalized instructions for the construction/operation of storage tanks and the clean-up of existing contaminated sites were recommended. Regulations on technical specifications and control of underground tanks to date are not harmonized within the EU. In order to reduce the risk for surface water, an obligation to obtain a permit in the framework of the directive 96/61/EG for overground storage tank systems was additionally demanded to be mandatory. This would allow for the control of the drainage of tank bottom water containing MTBE into surface water. This control would also be achieved by national requirements in the member states (Sur *et al.*, 2003).

The different emission controls of MTBE, which are already enacted, i.e. the most important EU directives concerning the composition of gasoline and the emission control from its distribution and use are summarized within the EU risk assessment (MEF, 2001).

The regulation of water quality in the EU is comparable to the water quality legislation in the U.S. Under the U.S. Safe Drinking Water Act (SDWA) and the Resource Conservation and Recovery Act (RCRA) many regulatory controls were mandated, that can also be found in the equivalent EU groundwater (80/68/EEC) and drinking water (98/83/EC) directives (Env.Exp., 2001). However, there are no European or national regulations for MTBE in drinking water, except for Denmark, which has set a limit value for MTBE in water of 30 µg/L. Other European countries are currently holding discussions to establish the guidelines and thresholds for groundwater (Schmidt *et al.*, 2001b; Sur *et al.*, 2003).

1.2.3. Germany

The maximum concentrations at working places (8h) (maximale Arbeitsplatzkonzentration, MAK) in Germany for MTBE was determined at 180 mg/m^3 (50 ppm) by the Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe (MAK commission) (MAK, 2000). Furthermore, this commission assigned MTBE to the groups 3B and C, which means that more research is needed to finally classify MTBE as human (non-)carcinogen (group 3B) and that

MTBE is not expected to show reproductive toxicity, when the maximum concentration of 180 mg/m^3 is not exceeded (group C) (see also Chapter 2.6.) (MAK, 2000).

In Germany, the existing requirements on the production, distribution and use of gasoline are seen by the German environmental agency (Umweltbundesamt, UBA) as prevention against widespread distribution of MTBE in the aquatic environment. The ordinance on installations for handling of substances hazardous to waters (Verordnungen über Anlagen zum Umgang mit wassergefährdenden Stoffen, VAwS) was enacted to limit accidental emissions. The hazardous substances are categorized into different classes. Pure MTBE was classified into Wassergefährdungsklasse 1, which represents the category with the lowest risk. Gasoline is classified into Wassergefährdungsklasse 3. This class implies the highest requirements regarding storage and distribution of the assigned substances. Thus, emissions of MTBE are limited due to the high classification of gasoline. The classification of MTBE into the lower Wassergefährdungsklasse 1 is only valid, if MTBE is transported, stored or used as pure substance.

The EU requirements to minimize the risks at gas stations, including double wall storage tanks, jacketed pipes, systems displaying leakages and overfilling, overfall basins and soil air sensors are largely implemented in the VAwS. Emissions to the air are limited by the German requirements related to the filling of tanks (Gaspendelung), transport, storage, automotive engineering (catalyst) and the emission of hydrocarbons. Further regulations which limit the emission of gasoline and MTBE were summarized by Pahlke *et al.* (2000) and Sur *et al.* (2003). Despite of the high technical requirements in Germany to prevent widespread adverse effects on the drinking water resources in Germany, the UBA concludes, that the use of the persistent MTBE as gasoline component is only an intermediate step (Sur *et al.*, 2003).

In Germany, only in the federal state of Berlin a clean-up level exists at 100 µg/L (Berliner Liste, 1996). However, meanwhile it is mandatory in the federal states of Bavaria and Rhineland-Palatinate to analyze groundwater from gasoline contaminated sites on MTBE and similar guidelines are prepared in Baden-Württemberg. The Länderarbeitsgemeinschaft Wasser (LAWA) has suggested a threshold of 5 µg/L for the valuation of MTBE releases into groundwater (Sur *et al.*, 2003).

2. PROPERTIES OF MTBE AND ITS BEHAVIOR IN THE ENVIRONMENT

2.1. Synthesis

MTBE or 2-methoxy 2-methyl propane (CAS-No. 1634-04-4, EINECS-No. 216-653-1) is commercially synthesized by the electrophilic addition of methanol to isobutene (Figure 2-1). Isobutene is a cheap by-product in refineries and can be obtained by steam cracker operation and fluid cracker operation. The production of isobutene by butane dehydrogenation or dehydration of TBA is cost-intensive. Methanol is derived primarily from natural gas (EFOA, 2004a). The synthesis of MTBE is catalyzed by an acidic ion exchanger resin (e.g. Ambelist, K2611). The regio-selectivity of the reaction follows the rule of Markownikow, since the H atom of the reagent with the structure H-R (Methanol) is added to the H-enriched C atom of the asymmetric double bond and the "R"-part of the reagent to the other C atom. The regio-selectivity may be explained by no-bond formulas that can be formulated for every H_{allyl} of the isobutene molecule (Figure 2-1). If in vicinity to C_β more H_{allyl} are located, a negative partial charge occurs at the center C_α.

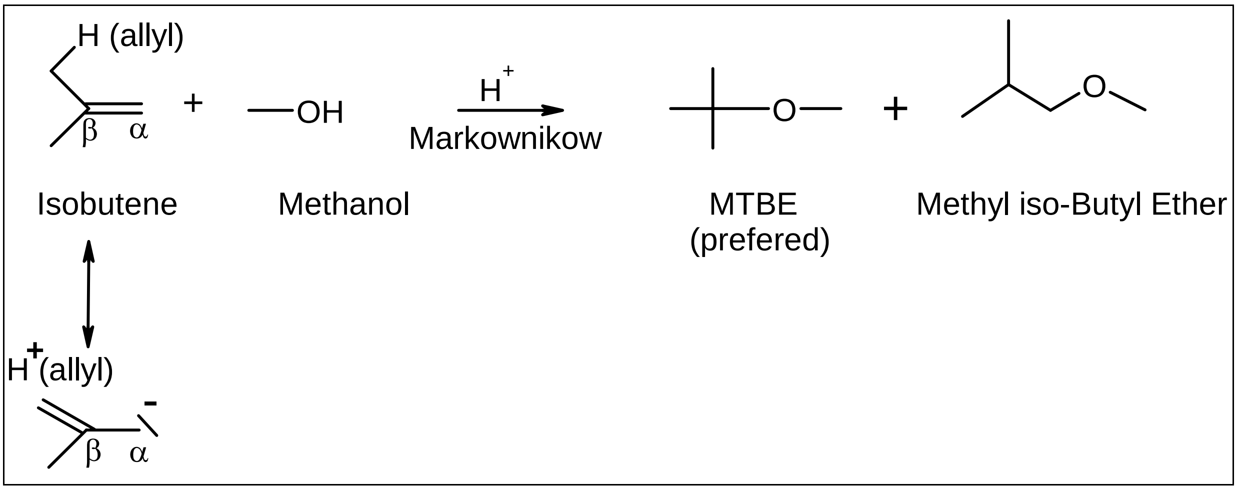

Figure 2-1: Synthesis of MTBE.

MTBE can also be synthesized by the reaction of methanol and TBA. The first synthesis of

MTBE was conducted in the year 1904 by a Williamson ether synthesis. Liquid MTBE can contain impurities (<1.5-0.1%) such as methanol, 2-methylpropan-2-ol, 2,4,4-trimethylpentene, C_4-olefins, aromatics, C_{4-6} parafins, 2,4,4-trimethylpent-1-ene, isobutene, di-isobutene (C_8H_{16} isomers), tri-isobutene ($C_{12}H_{24}$ isomers), *tert*-amyl methyl ether (TAME) and water (MEF, 2001).

2.2. Physico-Chemical Properties

Table 2-1 shows the environmentally relevant physico-chemical properties of MTBE, other oxygenates and benzene. At room temperature, MTBE is a chemically stable colorless liquid and has an antiseptic odor. MTBE does not tend to form peroxides during storage (MEF, 2001). It is flammable, combustible and has a research octane number (RON) of 117. Its motor octane number (MON) is 102. The use of gasoline oxygenated with MTBE results in 16-23% lower emissions of CO. The emission of hydrocarbons decreases about 18%. The addition of oxygenates to gasoline does not significantly influence the emission of NO_x and the emissions of aldehydes increase (Schifter *et al.*, 2001).

Compared to other oxygenates, MTBE has the lowest boiling point (55°C) and the highest vapor pressure (332 hPa at 25°C). Its vapor pressure is about three times higher than the vapor pressure of benzene (Table 2-1). With an increase of 20°C, the vapor pressure of MTBE approximately doubles (Achten, 2002). Organic compounds with a vapor pressure of 0.1 hPa (at 20°C) or higher belong to the group of the environmentally important volatile organic compounds (VOCs) (Bocchini *et al.*, 1999).

The water solubility and the Henry's law coefficient are important factors and determine the behavior and fate of a VOC in the environment to a large extent. MTBE is water soluble and soluble in most organic solvents. After the alcohol oxygenates, MTBE is the most water soluble gasoline constituent with a water solubility of 48 g/L (25°C) (Table 2-1). The solubility can be explained by the ability of MTBE to form at its oxygen atom hydrogen bonds with water. The alkyl chains of the other ether oxygenate (ETBE, TAME, DIPE) molecules are larger. The water solubility of MTBE decreases by a factor of 10 from pure MTBE (48 g/L) to MTBE in reformulated gasoline (4.7 g/L at 20°C) with 10% MTBE (w/w). The solubility of hydrocarbons in water from nonoxygenated gasoline is only about 0.09-0.12 g/L. The water solubility of MTBE at 5°C is about twice as high as its solubility at room temperature.

	Methyl *tert*-butyl ether **MTBE**	**Ethyl *tert*-butyl ether** **ETBE**	***tert*-Amyl methyl ether** **TAME**	**Diisopropyl ether** **DIPE**	**Methanol** **MeOH**	**Ethanol** **EtOH**	***tert*-Butyl alcohol** **TBA**	**Benzene**
CAS no.	1634-04-4	637-92-3	994-05-8	108-20-3	67-56-1	64-17-5	75-65-0	71-43-2
Molecular weight [g/mol]	88.15	102.18	102.18	102.18	32.04	46.07	74.12	78
Boiling point [°C]	55.2	72.2	86.3	68.2	64.6	78.3	82.4	80
Density [kg/L]	0.744	0.73	0.77	0.73 (20°C)	0.796	0.794	0.791	0.88
Vapor pressure [hPa]	332	203	91	200	168	79	56	101
Water solubility [g/L] pure	48	12	12	2	complete	complete	complete	1.760 (20-30°C)
from RFG (a=from conv.gasoline)	4.7 (20°C)	1.3 (20°C)	1.4 (20°C)	1.2 (20°C)	-	-	-	0.018 (a; 20°C)
Henry's law constant [atm m^3/mol]	$5.9*10^{-4}$	$2.7*10^{-3}$	$1.3*10^{-3}$	$4.77*10^{-3}$	$4.6*10^{-6}$	$5.2*10^{-6}$	$1.4*10^{-5}$	$5.6*10^{-3}$
log K_{OW}	1.24	1.74	1.55	1.52	-0.77	-0.31	0.35	2.12
logK_{OC}	1.05	0.95	1.27	1.13	0.44	0.20	1.57	1.92
MON	102	102	112	-	105	102	100	115

Table 2-1: Physico-chemical properties of MTBE, other gasoline oxygenates and benzene. Values are at 25°C. Adapted from Schmidt et al. (2001a) and Achten (2002).

The temperature dependent Henry's law coefficient (H) describes the partitioning of a compound between the water phase and the gas phase. MTBE behaves like a gaseous compound and therefore H can be calculated from water solubility and vapor pressure (Fischer *et al.*, 2004). For many organic compounds H decreases by a factor of two for every decrease in temperature by 10°C (Ligocki *et al.*, 1985). This is also valid for MTBE, with a H value of $5.38*10^{-4}$ m^3 atm/mol at 20°C and a H-value of $2.72*10^{-4}$ m^3 atm/mol at 10 °C (Fischer *et al.*, 2004). The varying experimental H values at different temperatures published by different authors is shown in Figure 2-2.

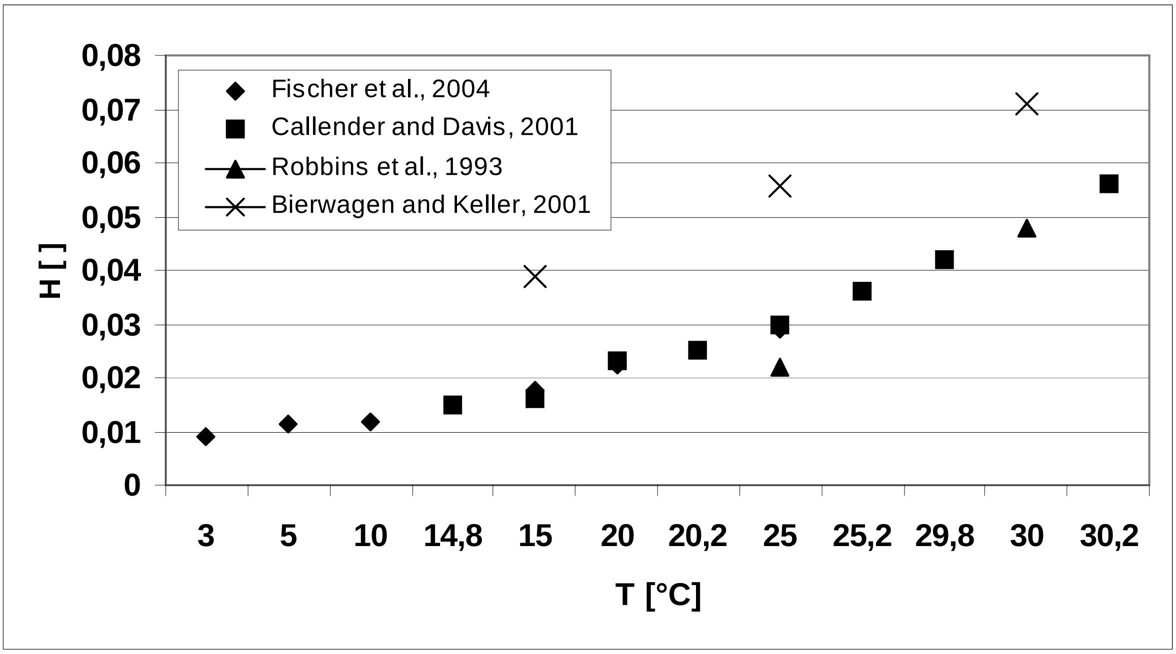

Figure 2-2: Published experimental Henry's law coefficients (H dimensionless) of MTBE at different temperatures. Values were summarized by Fischer et al., 2004.

Compared to benzene, the next water soluble conventional gasoline compound, MTBE is more water soluble by a factor of about 27 and its dimensionless Henry's Law constant of 0.022 (25°C) is lower by a factor of 10 (Benzene: 0.22 at 25°C). A compound with a value of 0.05 or higher is very volatile from water (Squillace *et al.*, 1996). The H values for MTBE indicate that MTBE tends to stay in the water phase, particularly at low temperatures. MTBE does not significantly accumulate in organisms and adsorbs only weakly to particles, which is expressed by the $\log K_{OW}$ and the $\log K_{OC}$ values (Achten, 2002). The temperature dependent conversion factors of MTBE are as follows:

1 mL/m^3 (ppm) = 3.94 mg/ m^3 or 0.254 mL/ m^3 (ppm) = 1 mg/m^3 at 0°C
(calculated from MAK, 2000)

1 mL/m^3 (ppm) = 3.66 mg/ m^3 or 0.273 mL/ m^3 (ppm) = 1 mg/m^3 at 20°C
(MAK, 2000)

1 mL/m^3 (ppm) = 3.57 mg/ m^3 or 0.280 mL/ m^3 (ppm) = 1 mg/m^3 at 25°C
(MEF, 2001).

2.3. MTBE Releases into the Aquatic Environment

MTBE can be emitted into the aquatic environment through a variety of sources. Point source releases are mainly related to leaking underground storage tanks (LUSTs) at MTBE production/formulation sites, to leaking pipelines and to gas stations. Despite of the reduced water solubility of MTBE from gasoline, large amounts of water can still be contaminated. If 4000 m^3 of water are mixed with one liter of gasoline containing 11% w/w MTBE, the resulting MTBE concentration is 20 µg/L (Squillace *et al.*, 1997), the lower limit of the USEPA drinking water advisory (USEPA, 1997). Concentrations higher than 20 µg/L can mostly be assigned to point sources (USEPA, 1999). Values of 1-5 µg/L were published by Schmidt *et al.* (2003) to distinguish between point and non-point sources. The release of MTBE into groundwater via point sources can result in MTBE groundwater concentrations in the mg/L-range. Contaminated sites with LUSTs may affect drinking water sources. One example is the often cited contamination of drinking water wells in Santa Monica (Chang and Last, 1999). The large number of perhaps 250,000 MTBE-LUSTs in the immediate vicinities of community water supply wells may represent a significant threat to drinking water in the U.S. over at least the current decade (Johnson *et al.*, 2000). MTBE contaminated sites also were reported in the EU, but statistics on MTBE contaminations related to LUSTs in the EU are not available.The EU risk characterisation arrived to the conclusion that risks for groundwater “are mainly related to leaking underground storage tanks and spillage from overfilling the tanks” (MEF, 2001). In Germany, a few sites with MTBE contaminated groundwater have been reported (Pahlke *et al.*, 2000; Effenberger *et al.*, 2001), e.g. the Leuna site described in Chapter 4.3.1. If contaminated groundwater dewaters into rivers, it may be seen as MTBE point source for surface water. Surface water is also affected by other MTBE point source releases. Release scenarios at MTBE production/formulation sites are described in the EU risk assessment (MEF, 2001). The release occurs via the treatment plants of the facilities. The wastewater of these effluents can contain MTBE in the mg/L-range (Brown *et al.*, 2001; MEF, 2001). Discontinuous MTBE releases into rivers by industrial plant effluents at industrial sites, where MTBE is used as solvent or reagent were reported by Achten *et al.* (2002b). MTBE is also emitted into rivers during shipping of large MTBE amounts, especially at leaking loading/unloading facilities. Since these releases are difficult to estimate, they were considered to be out of the scope of the EU risk assessment (MEF, 2001). Recreational water boating includes point and non-point sources of MTBE reaching surface water, since MTBE can reach the water via exhaust emissions during the use of the boats (Gabele *et al.*, 2000) or during refueling at marinas (An *et al.* 2002).

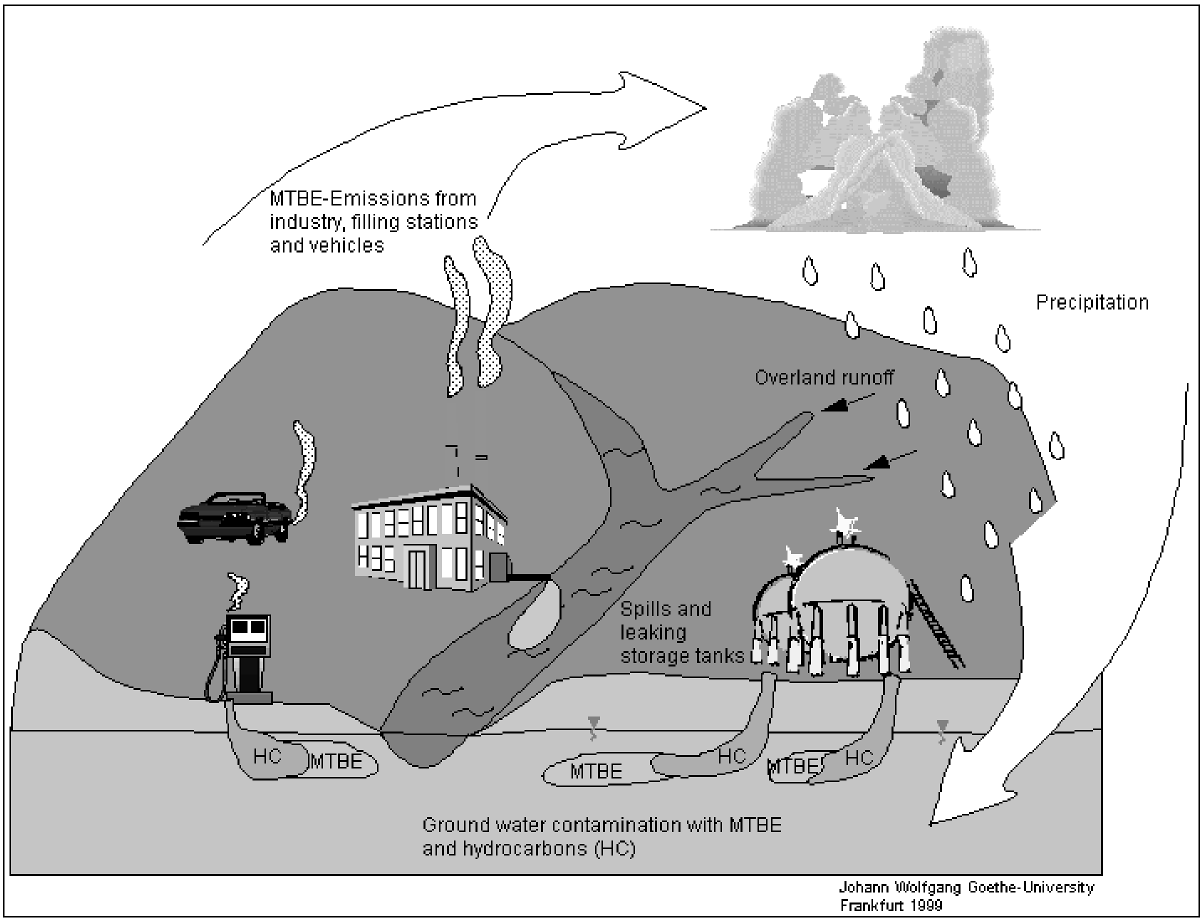

Figure 2-3: MTBE releases into the aquatic environment. The illustration does not include MTBE emissions via MTBE shipping and recreational boating.

Local MTBE surface water concentrations in the µg/L-range were measured (Reuter *et al.*, 1998; Dale *et al.*, 2000; Brown *et al.*, 2001; An *et al.*, 2002) and estimated (MEF, 2001) at sites, where recreational motor boating is carried out. Domestic wastewater from municipal sewage plants was also shown to contribute to MTBE contents in rivers and streams (Brown *et al.*, 2001; Achten *et al.*, 2002a). Municipal sewage plants are associated with urban runoff and subsequently with the diffusive atmospheric input of MTBE via precipitation. Therefore it is difficult to classify domestic wastewater effluents and urban runoff unequivocally as point or non-point sources. Urban runoff can contain MTBE that was scavenged in the atmosphere as well as MTBE from gasoline leakages on roads. The (urban) atmosphere was determined as diffusive source of MTBE in the U.S. and Europe (Pankow *et al.* 1997; Achten *et al.*, 2001c). MTBE in the atmosphere is assigned to evaporative emissions and incomplete combustion from motorways, gas stations, parking garages, refineries and chemical industry (Squillace *et al.*, 1996). Emissions to air from the use of gasoline were assumed to be the main source of MTBE releases to the environment (MEF, 2001). MTBE air emissions in Germany of 2285 t in the year 1999 were estimated (Pahlke *et al.*, 2000). Atmospheric inputs of MTBE via precipitation reach surface and groundwater.

2.4. Distribution of MTBE in the Environment

MTBE adsorbs only weakly to the soil compartment. Therefore, the distribution of MTBE between air and water phase determines the environmental fate of MTBE. Compartment modeling of MTBE in a generic environment using the equilibrium criterion (EQC) model (Achten *et al.*, 2002c) revealed for the Level I calculation at 10°C an equilibrium mass concentration of 87% MTBE in the air and 13% in surface water. The amounts that partition into soil and sediment compartments are below 0.02%. The equilibrium partitioning of Fugacity Level I calculations resulted in 93.9% of the MTBE distributed in the air and 6.045% in the water (at 20°C). At lower temperatures, the equilibrium partitioning is more shifted to the water phase (MEF, 2001), due to the lower Henry's law constant and the higher water solubility. Level III calculations in the EQC model allowed for the characterization of the sensitivity of different emissions into the four compartments. The "mode of entry" was shown to be more important for the MTBE input into water than for the input into air. The MTBE concentration in surface water was calculated to be almost exclusively the result of direct emission into water and MTBE migrates to the atmosphere by volatilization from the water (Achten *et al.*, 2002c). The travel distances of MTBE in rivers can range from 0.8 km for shallow and fast moving streams to more than 900 km for deep and slow moving rivers before half of the MTBE is volatilized (Pankow *et* *al.*, 1996). In addition to the Henry's Law constant, the air-water transfer kinetics of oxygenates like MTBE is also temperature dependent. During steady-state input conditions, the concentrations of MTBE and its degradation products in natural water bodies are influenced by temperature and wind speeds. The transfer of MTBE from the water phase into the air phase is relatively rapid. The half-life during calm conditions and temperatures lower than 10°C was calculated about 4-6 days (Arp and Schmidt, 2004).

The scavenging of MTBE by a precipitation amount of 2.5 cm at 20°C will remove less than 0.5% MTBE in the air (Zogorski *et al.*, 1997). The distribution of MTBE between atmosphere, surface water and subsurface were described in various studies (Pankow *et al.*, 1997; Baehr *et al.*, 1999a; Baehr *et al.*, 1999b; Bender *et al.*, 2000; Baehr *et al.*, 2001). The results suggest the (urban) atmosphere as source for MTBE concentrations of 0.25 μg/L and 0.1 μg/L in surface water and groundwater, respectively.

The behavior of MTBE at contaminated sites was summarized by Stocking *et al.* (1999). The gasoline components first migrate through the unsaturated zone between the surface and the water table. In some cases, the water table is reached by the non-aqueous phase liquid (NAPL). If the capillary columns are reached by the NAPL, MTBE migrates into the water phase due to its water solubility. Because MTBE has a higher vapor pressure than for example the BTEX components, it is assumed, that MTBE also volatilizes from the NAPL into the unsaturated zone air. MTBE subsequently migrates into the water phase due to the high gas phase concentrations and the low Henry's law constant. The factors influencing the speed of the migration into the water phase are the dimension of the contamination source, the saturation of the NAPL in the contaminated zone and hydrogeological factors. The assumption of a generally instant migration into the water phase therefore is not valid (Rixey *et al.*, 2000). In contrast to BTEX plumes, MTBE plumes that are formed within the groundwater were shown to be in many cases longer and less stable (more mobile), dependent on the hydrogeological relations (Happel *et al.*, 1998; Mace and Choi, 1998; Moran *et al.*, 2000) and the superimposition of biodegradation, dispersion and dilution. Because MTBE is only hardly degraded (see Chapter 2.5.), dispersion and dilution are assumed to be the main factors to reduce MTBE concentrations in the groundwater. In addition to the higher water solubility of MTBE compared to benzene (Table 2-1), MTBE also adsorbs only weakly to the underground matrix. In a sandy aquifer with an organic carbon content of 0.1%, only 8% of the MTBE mass are adsorbed, whereas 39% of the benzene mass and 72% of the ethyl benzene mass are retarded (Moran *et al.*, 1999).

2.5. Degradation

MTBE is difficult to biodegrade due to its molecular structure, i.e. the tertiary carbon atom, the ether bond and the absence of long alkyl chains. The major pathways that were proposed are the direct degradation to TBA and the transformation to *tert*-butyl formate (TBF) (Figure 2-4). The degradation to TBF occurs mainly in the atmosphere. The subsequent partitioning of TBF to atmospheric water may result in abiotic or biotic hydrolysis to TBA. At neutral pH and 22°C, the half-life time of the abiotic hydrolysis of TBF is 5 d (Church *et al.*, 1999). In the vadose zone, MTBE was observed to be transformed via TBF to TBA by certain soil fungi (Hardison *et al.*, 1997). The further pathways of degradation lead to a variety of products including 2-propanol (2-P), acetone (AT), formic acid, methyl acetate, formaldehyde, acetaldehyde, acetate and CO_2 (Howard *et al.*, 1996; Church *et al.*, 1997; Steffan *et al.*, 1997; USEPA, 2001).

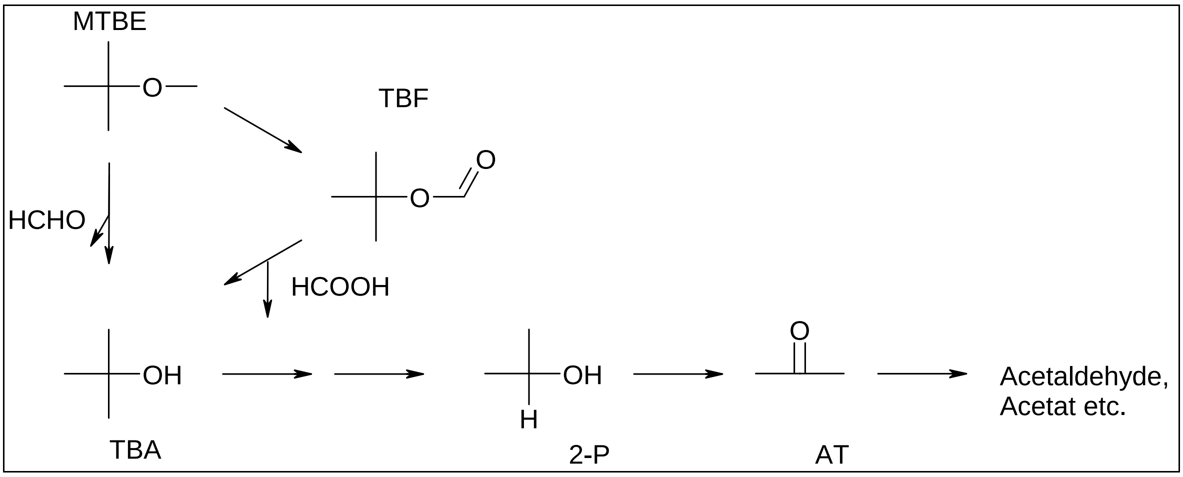

Figure 2-4: Proposed degradation pathways of MTBE by direct/indirect transformation to TBA (Hunkeler et al., 2001) and further proposed degradation pathway of MTBE/TBA by bacterial strain PM1 (USEPA, 2001).

2.5.1. Water and Soil

Generally, MTBE seems to be better degradable under aerobic conditions. Diverse microbial consortia were shown to have the ability to mineralize MTBE under aerobic conditions (Salanitro *et al.*, 1994; Deeb *et al.*, 2000; Hatzinger *et al.*, 2001; Francois *et al.*, 2002). The presence of oxygen generally enhances the biodegradation of MTBE and for significant MTBE degradation the oxygen content apparantly has to exceed a threshold of about 2 mg/L (Stocking *et al.*, 1999). Although MTBE was considered to be recalcitrant under anaerobic conditions due to its stable ether bond and *tertiary* alkyl part (Sulfita and Mormile, 1993; Bradley *et al.*, 1999), a few studies have evaluated its biodegradability under methanogenic (Yeh and Novak, 1994; Hurt *et al.*, 1999), sulfate-reducing (Somsamak *et al.*, 2001) and iron-reducing (Finneran *et al.*, 2001) conditions. Biodegradation of MTBE also occurred under different substrate conditions such as MTBE alone, MTBE with diethyl ether, MTBE with diisopropylether (DIPE), MTBE with ethanol and MTBE with BTEX (Deeb *et al.*, 2001; Pruden *et al.*, 2001). MTBE was also shown to be degradable as sole carbon and energy source and in the presence of cosubstrates like linear and branched short-chain alkanes or benzene (see Achten, 2002). If MTBE is used as sole carbon source, the cell yields are lower than those observed for aromatic hydrocarbons (USEPA, 2001). This is because some of the intermediate metabolites may inhibit cellular growth or MTBE serves as poor carbon and energy source (Stocking *et al.*, 1999). The presence of more easily biodegradable organic compounds may delay or inhibit MTBE biodegradation. A study on substrate interactions conducted by Deeb *et al.* (2001) suggested two independent and inducible pathways of MTBE and BTEX degradation. Furthermore, a severe and a partial inhibition of MTBE degradation by ethylbenzene/xylenes and benzene/toluene, respectively, could be observed. Subsequently, the biodegradation of MTBE at contaminated sites would be delayed, until MTBE has migrated beyond the BTEX plume, if other subsurface microbial communities behave similar to the culture used in the study (Deeb *et al.*, 2001). Surface water sediments may be a sink for MTBE contents in surface water, since MTBE was shown to be degradable in surface water sediments under aerobic and anaerobic conditions (Bradley *et al.*, 1999; Bradley *et al.*, 2001a; Bradley *et al.*, 2001b). Although MTBE was shown to be degradable in laboratory experiments, there is no convincing evidence that MTBE biodegradation occurs rapidly in the field under natural conditions (Deeb *et al.*, 2001). The evidence for biodegradation of MTBE at field sites was observed by Borden *et al.* (1997), Mace and Choi (1998), Schirmer and Barker (1998), Bradley *et al.* (1999), Landmeyer *et al.* (2001), Wilson *et al.* (2000) and Wilson *et al.* (2002).

The different remediation technologies used for cleanup of MTBE contaminated (ground)water are discussed elsewhere (Stocking *et al.*, 1999; Woodward and Sloan, 2002; DSCWEB, 2004) and recently demonstrated and ongoing research in promising remediation technologies can be found in publications of Major *et al.* (2003) and Martienssen and Schirmer (2003). Because in the present study also finished drinking water samples were analyzed for their MTBE content, the behavior of MTBE during drinking water processing including bank filtration is important. The efficiency of MTBE removal during drinking water treatment with technologies commonly used in Germany was investigated in laboratory-scale experiments (Baus *et al.*, 2003). MTBE is removable by aeration, but as a result of its low Henry constant very high bubble columns would be required. This would not be economically practible. The insufficient adsorption characteristics of MTBE limit the use of adsorption on activated carbon to remove MTBE from water in waterworks operating with common filtration cycle times. Technologies like advanced oxidation processes (AOPs) (e.g. Ozone/H_2O_2) are able to fully eliminate MTBE from natural waters but the technical and financial efforts would be enormous. The comparitative measurement of raw water, bank filtered water and finished drinking water in waterworks (Sacher, 2002) supported the findings in laboratory-scale experiments. The waterworks investigated uses bank filtration, ozonation and activated carbon filtration. MTBE could be found in all bank filtrated water samples and in the majority of the drinking water samples (Sacher, 2002) (see also Chapter 4).

2.5.2. Air

The major pathway of MTBE degradation in the atmosphere is the attack by the hydroxyl radical (Smith *et al.*, 1991), although MTBE can also be degraded by various processes including photolysis and reactions with ozone and nitrate radicals (Squillace *et al.*, 1996). The reaction pathway of MTBE with the hydroxyl radical in the presence of NO_x is illustrated in Figure 2-5.

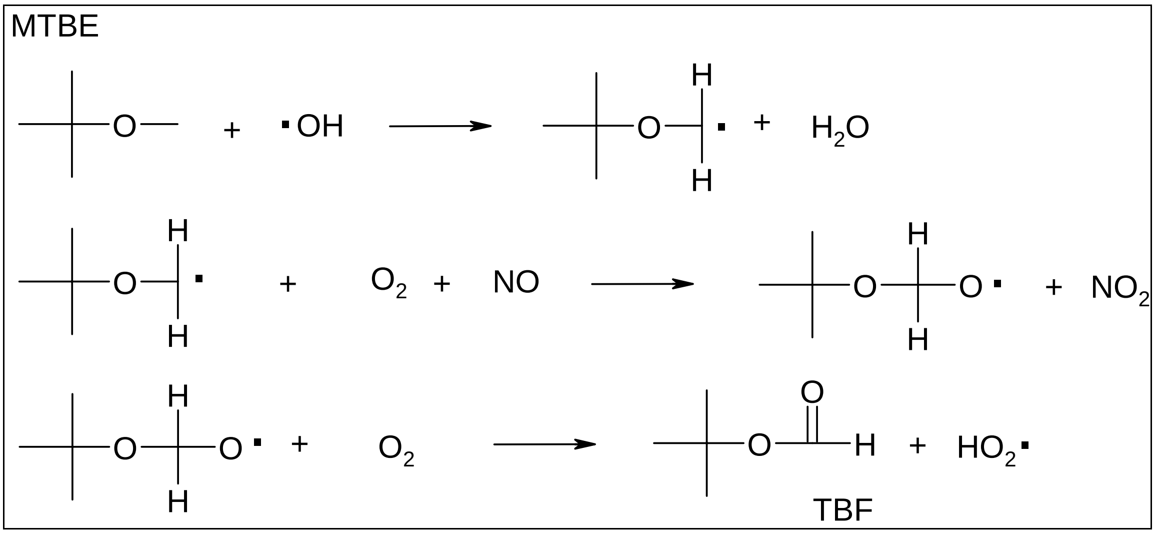

Figure 2-5: Reaction pathway of MTBE by hydroxyl radical attack in the presence of NO_x, proposed by Smith et al. (1991).

The rate constant of the MTBE degradation published by different authors ranges from 2.84-3.09*10^{-12} cm^3/molecule*s at 298 K (MEF, 2001). The atmospheric half-life time of 3-6 d depends on the atmospheric conditions, in particular on the atmospheric hydroxyl radical concentration. Studies on the atmospheric degradation of MTBE carried out in photoreactors or smog chambers (Becker *et al.*, 1998) revealed TBF yields of MTBE oxidation reactions in the presence or absence of NO_x of 50-90% and 61%, respectively. The formation of formaldehyde, methylacetate, carbonyl compounds, alcohols and, in the absence of NO_x, hydroperoxides could also be observed. TBF reacts slowly with the hydroxyl radical, a rate constant of $7.4*10^{-13}$ cm^3/molecule*s was measured by Smith *et al.*(1991).

2.6. Toxicity

The potential health effects of MTBE have been discussed in many studies and still the toxicity of the ether has not been finally evaluated. U.S., EU and worldwide institutions such as the USEPA, the World Health Organization (WHO), the European Center for Ecotoxicity and Toxicity of Chemicals (ECETOC) and the Ministry of the Environment Finnland (MEF) concluded that "it appears unlikely, that MTBE alone induces acute health effects in the general population under common exposure conditions" (WHO, 1998).

Acute human health effects like nausea, dizziness and headaches have been reported by people exposed to gasoline vapors. These symptoms could not be assigned clearly to MTBE (Toccalino *et al.*, 2004). MTBE is not considered as skin irritant and it was shown to be moderate irritant in the rabbit eye. MTBE leads to irritation of the mucous membranes and to adverse effects on the central nervous system at exposure levels higher than 50 ml/m^3 (MAK, 2000). The acute toxicity in animal studies was low, the LD_{50} (oral exposure) is 4000 mg/kg, the LD_{50} (dermal exposure) and the LC_{50} (inhalation) were determined at >10,000 mg/kg and 100,000 mg/m^3, respectively. The human health effects caused by long-term inhalation and oral exposure to MTBE are unknown (MAK, 2000; Toccalino *et al.*, 2004). Because of adverse effects on the liver, the NOAEL (no observed adverse effect level) for mammals was assigned to 800 ppm (inhalation) and 300 mg/kg/d (oral exposure). These NOAELs are important for MTBE exposures via the environment, but they were obtained only from sub-chronic 90 days studies (Sur *et al.*, 2003). At higher concentrations adverse effects on the central nervous system and the hemogram were observed in animal studies (rats and mice). Further effects were nephropathy and increased organ weights (liver, kidney, adrenal) (MAK, 2000). Carcinogenic effects were observed in rats and mice at inhalation and oral exposure higher than 300 ppm and higher than 250 mg/kg, respectively. It is supposed, that the carcinogenic effects are not due to genotoxic mechanisms. All *in vivo* studies on the genotoxicity of MTBE were negative up to toxic dose rates (MAK, 2000). The NOAEL for carcinogenic effects in mammals was established at 400 ppm (inhalation exposure) and 250 mg/kg/d (oral exposure) (Sur *et al.*, 2003). The conclusions that have been drawn from the animal cancer studies include a range of classifications. The National Toxicology Program (USA) has not recommended to list MTBE in the report on carcinogens, whereas the USEPA concludes that "MTBE poses a potential for human carcinogenicity at high doses" (Toccalino *et al.*, 2004). The MAK commission assigned MTBE to the class 3B, which means that more research is needed to classify MTBE finally as (non-)human carcinogen. On the basis of the available information, MTBE is not classified as human mutagen and no fertility or reproductive toxicity is expected (MAK, 2000; Sur *et al.*, 2003). The drinking water level in the range of 20-40 µg/L was set by the USEPA with respect to the taste and odor characteristics of the drinking water (USEPA, 1997) and the levels are orders of magnitude lower than the exposure levels in which cancer or non-cancer effects were observed in animal studies. MTBE concentrations as low as 2-2.5 µg/L may lead to objectionable taste and odor detections by sensitive subjects (Borden *et al.*, 2002). MTBE is metabolized by Cytochrome-P450 to formaldehyde and TBA. The toxicities of these substances also have to be considered and may cause some of the adverse effects (MAK, 2000).

Aquatic ecotoxicity data on MTBE are in the mg/L-range for freshwater and marine organisms (MEF, 2001; Werner *et al.*, 2001; Mancini *et al.*, 2002; Rausina *et al.*, 2002). The measured surface water concentrations in the U.S. are not seen to pose a risk to aquatic organisms (Mancini *et al.*, 2002). The predicted no effect concentration (PNEC) for the aquatic compartment was calculated to 2.6 mg/L within the EU risk assessment (MEF, 2001). Recently, MTBE was reported to increase the photoinduced toxicity of fluoranthene and potentially other PAHs in aquatic environments due to enhanced bioconcentration factors. This effect was observed at concentrations of 20 µg/L and 40 µg/L for fluoranthene and MTBE, respectively (Cho *et al.*, 2003).

2.7. Economical and Environmental Aspects of MTBE Substitutes

All gasoline oxygenates listed in Table 2-1 and Figure 2-6 are High Production Volume Chemicals according to the Organisation for Economic Cooperation and Development (OECD). After MTBE, ethanol is the second most important gasoline oxygenate with a production amount of 8.4 Mio t in the U.S. in 2003 (RFA, 2004). The production will increase considering the ban of MTBE from gasoline in many states of the U.S. including California (see Chapter 1.1.1.).

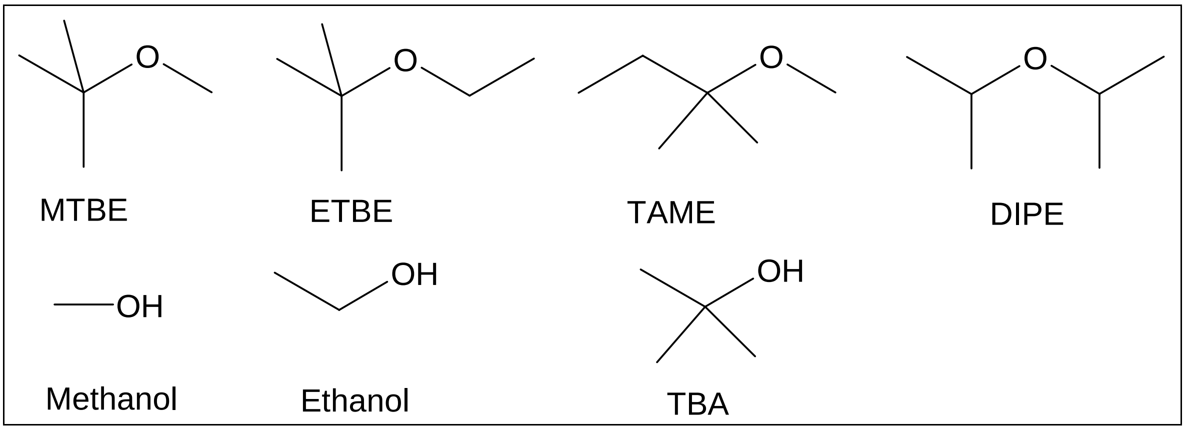

Figure 2-6: Structures of gasoline oxygenates.

The dominant oxygenate replacement that is currently considered and used is ethanol. Alcohols are rarely used as gasoline oxygenates in the EU, but the EU requirements to increase the market share of biofuels may also raise the production of gasoline ethanol in the EU. ETBE, TAME and DIPE are considered as substitutes for MTBE in the EU, but apart from TAME in Finnland (0.1 Mio t/a) and ETBE in France (0.16 Mio t/a) and Italy, these substances were not yet used in large amounts, since they cannot compete economically with MTBE (Sur *et al.*, 2003; Schmidt *et al.*, 2001a). However, similar to ethanol, the amounts of ETBE produced may increase due to tax incentives (Schmidt *et al.*, 2001b). Some petroleum companies currently are proposing and enhancing the substitution of MTBE by ETBE (Shell, 2003; Stupp, 2004). The ethyl component of ETBE would originate from the reaction of bioethanol with isobutene.

Similar to MTBE, the other named fuel oxygenates have higher water solubilities, lower Henry's law constants and lower sorption constants than other fuel-related compounds, e.g. benzene (Table 2-1). Subsequently, these compounds will also reside in air and water rather than in soil or biota (Schmidt *et al.*, 2001a). The main differences of the ether oxygenates MTBE, ETBE, DIPE and TAME in environmental properties can be found in the dissertation of Achten (2002). Some alternatives (ETBE, TAME and DIPE) to MTBE were recently shown to have generally higher Henry's law constants. This implies that they will partition more readily into the air phase, where degradation and dilution are the most effective (Arp and Schmidt, 2004).

ETBE as favored substitute for MTBE has a four times lower water solubility, a lower boiling point and a lower vapor pressure. These properties are also advantages in terms of precaution to avoid a widespread possible distribution in the aquatic environment. However, the advantage of ETBE over MTBE is not yet proven with respect to their behavior in groundwater. ETBE is expected to have a similar low biodegrdability, due to its similar molecular structure (Sur *et al.*, 2003).

The use of ethanol instead of MTBE as gasoline oxygenate implies some economical and logistic disadvantages. The minimum oxygen contents of gasoline in some regions in the U.S. can be fulfilled with ethanol instead of MTBE, indeed. However, in the EU, the ethanol content of gasoline is restricted to 5% w/w, since the compatibility of ethanol-blended gasoline with polymer coatings and gasoline feed lines is limited. This limits the use of ethanol to produce gasoline with high octane values, e.g. Super Plus (Sur *et al.*, 2003). The hygroscopic nature of ethanol also causes logistic problems. If ethanol-blended gasoline (4-5 % v/v) is stored, it tends to separate from the gasoline (Sur *et al.*, 2003). In addition, an ethanol-blended gasoline may bring water from water vapors (e.g. in pipelines) into solution and the gasoline will be rendered unusable. Because of these problems, ethanol is transported separately from gasolione, typically by rail car or truck. The blending is then carried out at the distribution terminal. In terms of economical considerations, the volume losses of gasoline caused by the replacement of MTBE by ethanol, plays an important role. The RFG oxygen requirement of 2.1% w/w in the U.S. can be met with 5.5% v/v ethanol instead of 11% v/v MTBE. Ethanol increases the vapor pressure of gasoline, in contrast to MTBE, which has only a small effect. These blending properties of ethanol can decrease the volume of the produced gasoline, since two liters of MTBE are substituted by about one liter of ethanol, since low cost high vapor pressure components such as butane and pentanes must be removed from the RFG pool and since heavy, high boiling temperature volumes have to be removed. The latter must be carried out in order to counter the loss of high vapor pressure, low boiling temperature components and the net reduction in light oxygenate volume. The net volume loss of MTBE must be replaced by high-octane blend components such as alkylate and iso-octane. The availability of these components is limited. These factors and in addition the above mentioned logistic changes which accompany the shift from MTBE to ethanol, are expected to increase the RFG prices (Lidderdale, 2003). A further disadvantage of the ethanol use is the formation of the air contaminant acetaldehyde. An increase of hydrocarbon emissions and an increase of ozone pollution was assigned to the anticipation of the MTBE replacement in California by ethanol (Sur *et al.*, 2003; EFOA, 2004). However, in terms of groundwater prevention, ethanol has some favorable advantages compared to MTBE. A recent study by Dakhel *et al.* (2003) revealed a concomitantly disappearence of ethanol, benzene and all other petroleum hydrocarbons except isooctane and MTBE from aerobic groundwater due to biodegradation. The study was carried out under outdoor conditions typical for winter in temperate regions.

TBA is of environmental importance, since it is the main degradation product of MTBE in aqueous systems (Schmidt *et al.*, 2001a).

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3. ANALYTICAL METHODS

In the present study, environmental water samples were collected and analyzed for their MTBE content. Before investigations on MTBE in the aquatic environment can be conducted, it is important to know about the MTBE contents that are added to gasoline in the corresponding region or country, where the investigation is carried out. This information is useful for subsequent calculations, estimations, modeling and comparisons to other MTBE data, e.g. from the U.S. Oxygenates in gasoline can be determined by a variety of methods, a method using gas chromatography (GC) was described by Achten and Püttmann (2000). From that work and in addition from gasoline data published by the Umweltbundesamt (Sur *et al.*, 2003), MTBE concentrations in German gasoline were known. They served as sufficient basis for some of the implications that were made from results obtained throughout the present study. Therefore, no measurements of MTBE in gasoline were conducted and the methods to determine MTBE in gasoline are not described within this work.

3.1. Analysis of MTBE in Environmental Water Samples

Schmidt *et al.* (2001a) gave an overview on the common methods to determine oxygenates and in particular MTBE in environmental water samples. The methods consist of enrichment, separation and detection of MTBE. The enrichment step is generally seen as the most critical step in all methods. The complete method used for the present study is described in Chapter 3.2.

3.1.1. Extraction/Enrichment

The method that requires no sample preparation and only low sample volumes (0.001-0.1 mL) is direct aqueous injection (DAI) of the sample onto the chromatographic column. All DAI applications require a wide-bore precolumn and sometimes polar columns are used, to retain water more strongly. The analytes (MTBE) then are eluted earlier than water. Church *et al.* (1997) and Schmidt *et al.* (2002) obtained method detection levels (MDLs) for MTBE as low as 0.1 μg/L and <0.2 μg/L, respectively. The method allows for the simultaneous determination of alcohols and ethers. The disadvantages of DAI are the phase deterioration after multiple water injections and the very efficient pumps that are required when mass spectrometry (MS) is used as detection system (Schmidt *et al.*, 2001a).

The low sensitivity limits the direct static sampling of the headspace (HS), when MTBE is analyzed in environmental water samples. This method can easily be automated and is suitable for contaminants with high Henry's law constants or samples that are highly contaminated with MTBE. Especially for alcohols static HS samping is rather less suitable, since the Henry's law constants of the alcohols are too low (see Table 2-1). Robbins et al (1993) used the static headspace method to determine the Henry's law constant for MTBE and obtained a MDL of 4.87 µg/L.

Purge and Trap (P&T) enrichment of analytes is used for purgeable analytes that have a Henry's law constant sufficient for an efficient stripping from the aqueous phase. This method combined with MS detection is used as standard procedure by the USEPA (Method 524.2) to analyze more than 60 VOCs including MTBE simultaneously. The MDL of this method for MTBE is 0.09 µg/L. MDLs of 0.06 µg/L and 0.01 µg/L were reported by Raese *et al.* (1995) and Barcelo *et al.* (2003), respectively. The method described by Barcelo *et al.* (2003) allows for the simultaneous determination of MTBE, its degradation products and other VOCs. The disadvantages of P&T are the susceptibility for contaminations and the complex system that is required for purging the VOCs with helium and for cryofocussing the analytes on top of the GC column (Schmidt *et al.*, 2001a).

A cheap and simple method for the determination of MTBE in environmental water samples is solid phase microextraction (SPME). Some aspects of this method are described here and in Chapter 3.2.3. more detailed, since this method was used in the present study. The method can either be used to extract the analytes directly from the water sample or in the headspace above the sample (HS-SPME). The extraction efficiency in the direct mode is determined by the partitioning between the water phase and the fiber coating. In the headspace mode the analytes partition between the water and air phase and between the air phase and the fiber coating. In both cases, extraction parameters such as ion strength of the water solution, temperature of the sample and the fiber, stirring of the sample, sample volume, volume of the extraction vial and the type of fiber coating used can be optimized (Zhang *et al.*, 1996). The method is very sensitive and appropriate for ultra-trace analysis of MTBE in the ng/L-range. The poor reproducibility of the method can be compensated by using an isotopically labeled internal standard (Schmidt *et al.*, 2001a). Since a wide range of fiber coatings is commercially available, the method is very popular for analyzing a variety of volatile and semivolatile compounds (Schmidt *et al.*, 2001a). The direct extraction of MTBE in water revealed a MDL of 10 ng/L (Achten and Püttmann, 2000). Cassada *et al.* (2000) obtained MDLs of 8 ng/L for MTBE and 1.8 µg/L for TBA. The method to analyze MTBE was further improved by optimizing the extraction parameters for the

HS-SPME (Achten *et al.*, 2001). The MDL still was 10 ng/L and due to the HS extraction, the matrix effects were minimized. These matrix effects lead to shorter lifetimes of the fiber and to instability of the MS system due to contamination of the ion source by low volatile organic compounds and water.

Because of the high sensitivity, the (HS-)SPME method is together with P&T the most suitable method to determine MTBE in environmental samples even at concentrations below 100 ng/L. The two methods may be used complementary, since for example in the direct SPME mode high levels of monoaromatic compounds limit its use due to dropping of the response of the internal standard (Black and Fine, 2001). The results of an interlaboratory study (Schumacher *et al.*, 2003) indicated comparable data quality for P&T and SPME. DAI also was shown to be an accurate method to determine MTBE in water in the ng/L-range. Static headspace extraction showed lower accuracy. The results arranged according to quantitation technique revealed higher precision of the methods when internal standards were used showing 10% standard deviation of recoveries than methods where external standards were used showing 42% standard deviation of recoveries (Schumacher *et al.*, 2003). The performance of the method used within this study can be found in Chapter 3.2.7.

3.1.2. Separation

The separation of the analytes (MTBE) is generally carried out by gas chromatography. The type of column used depends on the applied enrichment technique, the sample matrix and the kind of injection. A megabore column (e.g. DB-624, J&W Scientific) is used in EPA method 524.2, allowing the separation of a large number of contaminants. For DAI applications, often polar columns are specified (DB-WAX like, J&W Scientific). In most HS and SPME applications, non-polar columns (D-1 and DB-5 like, J&W Scientific) are used. The separation of MTBE from the coeluting gasoline related compounds 2,3-dimethylbutane and in particular 2-methylpentane is critical (Schmidt *et al.*, 2001a). Columns that were shown to be able to resolve the signals of MTBE and 2-methylpentane to an acceptable extent are DB-MTBE (J&W Scientific) (George and Vickers, 1999) and a FS-SE-54-CB-5 (50 m, 0.32 mm inner diameter) column with a film thickness of 5 µm (Chromatographie Service, Langerwehe) (Achten *et al.*, 2001d).

3.1.3. Detection

Flame ionisation detection (FID) and MS are the commonly used detection methods for determining oxygenates (MTBE) in water samples. Although photoionisation detection (PID) might be a cheap alternative to MS detection, its use in oxygente analysis was only rarely described (Schmidt *et al.*, 2001a). Atomic emission detection (AED) and Fourier transform infrared spectroscopy (FTIR), which does not require a separation step, are difficult to improve for environmentally relevant concentrations (Schmidt *et al.*, 2001a).

The advantages of FID are its inexpensive and easy use. For trace analysis, its selectivity and sensitivity are too low. Therefore, FID is appropriate for samples with a limited number of compounds and rather high contaminations (Schmidt *et al.*, 2001a). Identification of compounds is critical, e.g. regarding the superimposition of MTBE and 2-methylpentane. If MS is used as detection method, its application in the full scan mode provides the possibility to check the signals with respect to superimpositions. The compounds can be unequivocally identified and if the target compounds are known, the MDL can be lowered by a factor of 100-1000 by using the selected ion monitoring (SIM) mode. Although the aquisition and the maintaining of the MS system are expensive, its selectivity and sensitivity make it the predominant detection method for MTBE analysis in environmental water samples at background concentrations. The only mode described for the ionisation of oxygenates in the MS detector is electron impact (EI) ionisation. When gasoline oxygenates are analyzed, no molecule ions (except for methanol) can be observed. MTBE yields after α-cleavage the fragment $(CH_3)_2COCH_3^+$, which is also the quantitation ion m/z 73. The confirmation ions are m/z 57 and m/z 43.

3.2. Determination of MTBE in Water Samples by HS-SPME Combined with GC/MS

Since in the present work mainly water samples with expected MTBE concentrations in the ng/L-range were analyzed, the method of choice was HS-SPME extraction as enrichment technique and GC-MS as separation and detection method. The comprehensive optimization and evaluation of the method was described by Achten *et al.* (2001c).

3.2.1. Sampling

The samples were collected with respect to the standard water sampling techniques for VOCs described by Koterba *et al.* (1995). The samples were stored in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. They were stored and transported at 4° C and analyzed within three weeks. During sampling and transport of water samples field blanks were present and analyzed parallel. Details of the different sampling campaigns, i.e. the collection of drinking water, surface water, rain water, snow, groundwater and wastewater are described in the corresponding Chapters 4.-8.

3.2.2. Standard Solutions

MTBE calibration solutions in the range of 20-5000 ng/L and solutions of isotopically labeled d_3MTBE at concentrations of 10 µg/L were prepared. Stock solutions of 2000 µg/mL MTBE in methanol (Sigma-Aldrich) and pure d_3MTBE (>99%, Sigma-Aldrich) in the highest commercially available purity were used to prepare the MTBE calibration standards in two steps. The first dilution was carried out using methanol and only the preparation of the final standard solutions were made in distilled water. The used stock solutions, the distilled water and the used vials were pre-cooled to 4°C in order to minimize losses of the ether through evaporation. Since no standard procedures were available to prepare MTBE calibration solutions, the handling of the syringes and the dilution steps were carried out with respect to the standard procedures for BTEX compounds (DIN 38 407). The first dilution in methanol was conducted by pushing the needle of the syringe a few milimeters into the methanol and pushing the plunger of the syringes very gently in several increments. The final dilution step in water was carried out by stirring the water and pushing the needle of the syringe into the funnel that was generated by the stirring. The standard solutions were similar to the samples cooled to 4°C and used within 4 weeks.

3.2.3. Headspace-Solid Phase Microextraction (HS-SPME)

Before the extraction, 4 ml of the sample or standard solution was added to a 10 mL extraction vial that contained already NaCl in the highest purity commercially available (>99.5%, Merck), resulting in a NaCl concentration of 10% w/w. In addition, 40 µL of the internal d_3MTBE standard solution was added, so that the concentration of the internal standard was 100 ng/L. The vials were closed with septa (Dichtring Sil/PTFE blau-transparent 3.0 mm, Loch 11 mm, Chromatographie Zubehör Trott, Kriftel) of two different thicknesses in order to ensure a tight seal at the outer ring and ease of piercing by the SPME sampling holder in the inner part. During the extraction, the immersion depth of the fiber into the headspace of the water sample was 0.8 cm. For the SPME, a manual sampling holder equipped with a 75 µm polydimethysiloxane/carboxene fiber (PDMS/carboxene) from Supelco was used and cooled to 0°C by a cryostat (Haake, Berlin). The sample was stirred at 895-900 rev/min with a magnetic stirring bar (3 mm, Supelco). The sample vial was placed in a water bath. The magnetic stirring unit also served as heater. During the extraction, the sample was heated to 35°C. The extraction time was 30 min. Since the fiber had no direct contact to the water sample, the fiber could be used for up to 1000 extractions (Achten *et al.*, 2001c), but generally its lifetime was about 40-100 extractions. Magnetic stirring bars, sample and extraction vials and the used NaCl were heated before use to 130°C at least for 5 h, since MTBE might have been present in the laboratory air.

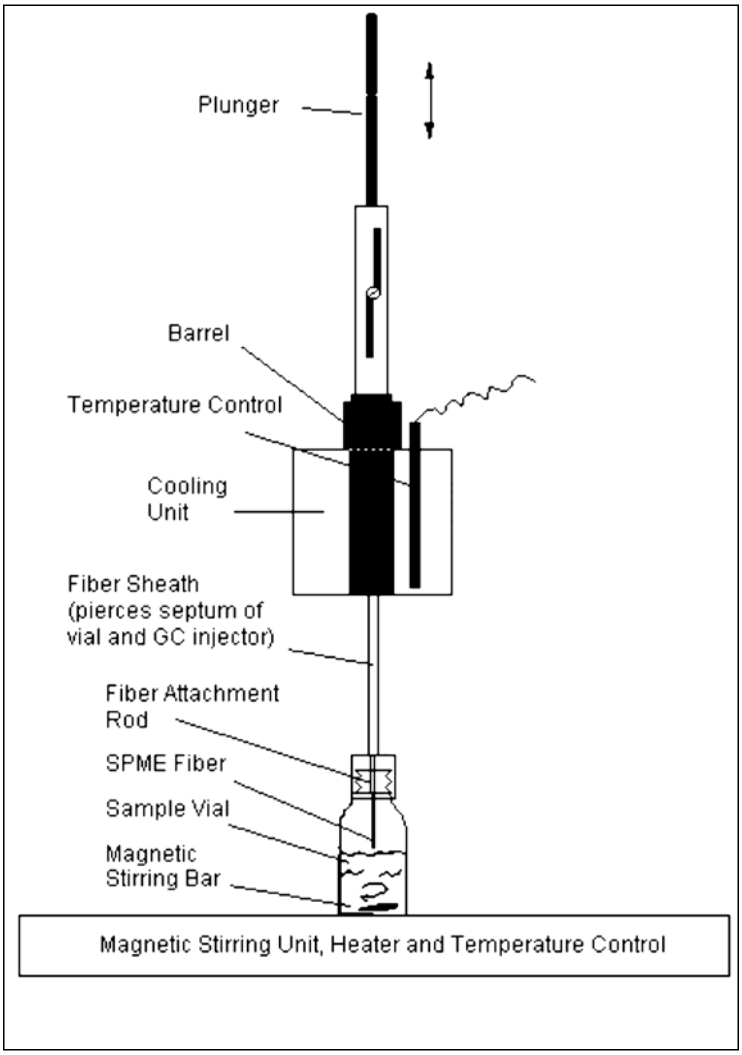

Figure 3-1: Arrangement of the different components during the HS-SPME.

3.2.4. Gas Chromatography (GC)

The thermal desorption from the fiber onto the chromatographic column was carried out by inserting the fiber into the injector of the GC at an immersion depth of 4 cm. The fiber remained in the injector for 10 min to be conditioned for the next extraction. The septum of the injector port had to be changed regularly, since the needle containing the SPME fiber is thicker than for example a Hamilton syringe. The temperature of the injector was 260°C and it was used in the split mode at a split ratio of 1:10. A SPME liner (Supelco) with an inner diameter of 0.8 mm was used. After an initial temperature of 50°C, that was held for 1 min, the GC column was heated at a rate of 10°C/min to 190°C. The final temperature was held for 20 min. Helium served as carrier gas at a constant pressure of 70 kPa. The GC was a Trace GC 2000 series (Thermo Quest, Egelsbach). The column originally used was a 50 m FS-SE-54-CB-5 capillary column (Chromatographie Service, Langerwehe) with a film thickness of 5 µm. This large film thickness led to bleeding of the column and fast contamination of the ion source in the MS detector. Therefore this column was replaced by a J&W Scientific DB-624 column (60 m, 0,32 mm inner diameter) with a film thickness of 1.8 µm.

3.2.5. Mass Spectrometry (MS)

The GC was coupled to a MS (Voyager, Thermo Quest, Egelsbach). The peak identification and quantitation was carried out with Xcalibur 1.0 software. The MS was used in the full scan mode (m/z 40-600) and with EI ionisation (70 eV). The MS was tuned to otimize signals from m/z 40-125. MTBE was identified by the fragments m/z 73, 57 and 43 (Figure 3-3). The quantitation was carried out by mass chromatography of the fragments m/z 73 and m/z 76 (internal standard d_3MTBE) (Figure 3-5) in the full scan mode. The full scan mode allowed for the check of the MTBE signals with respect to superimposition by other compounds. The detection limit was defined by a signal to noise ratio of 10:1.

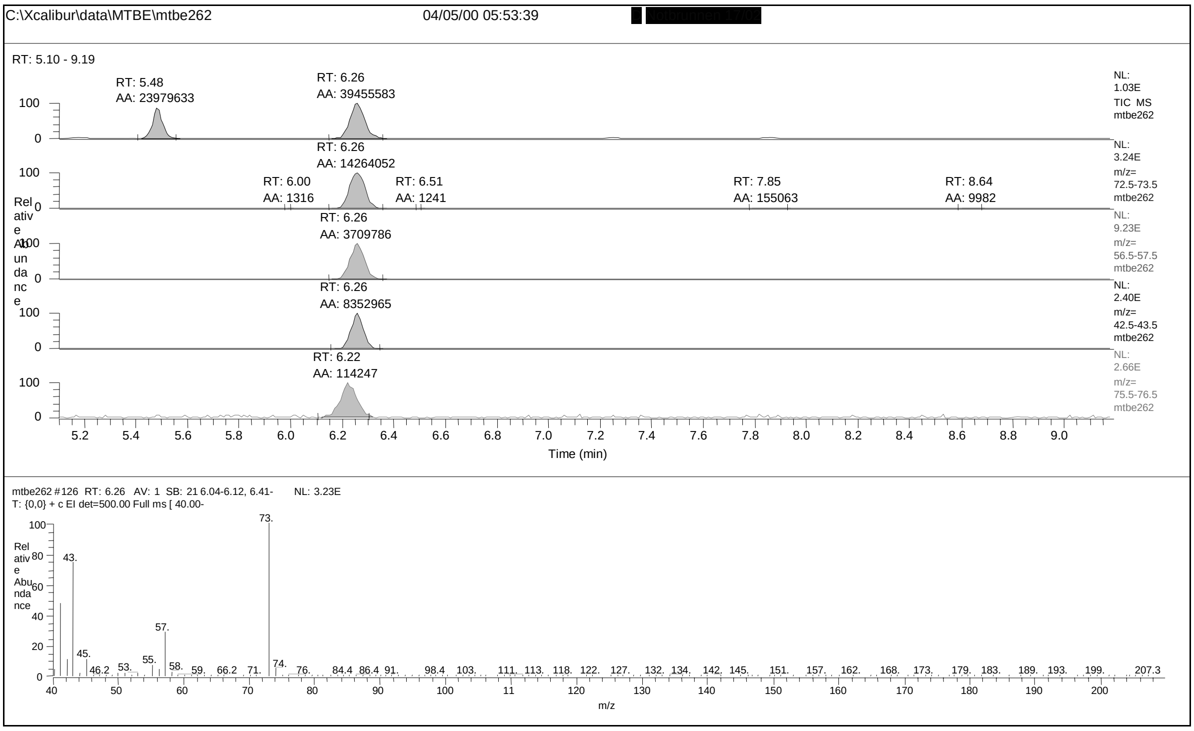

Figure 3-2: Total ion current (TIC) and mass chromatogram of m/z 73, 57, 43 (MTBE), m/z 76 (d_3MTBE) and mass spectrum of MTBE in a groundwater sample.

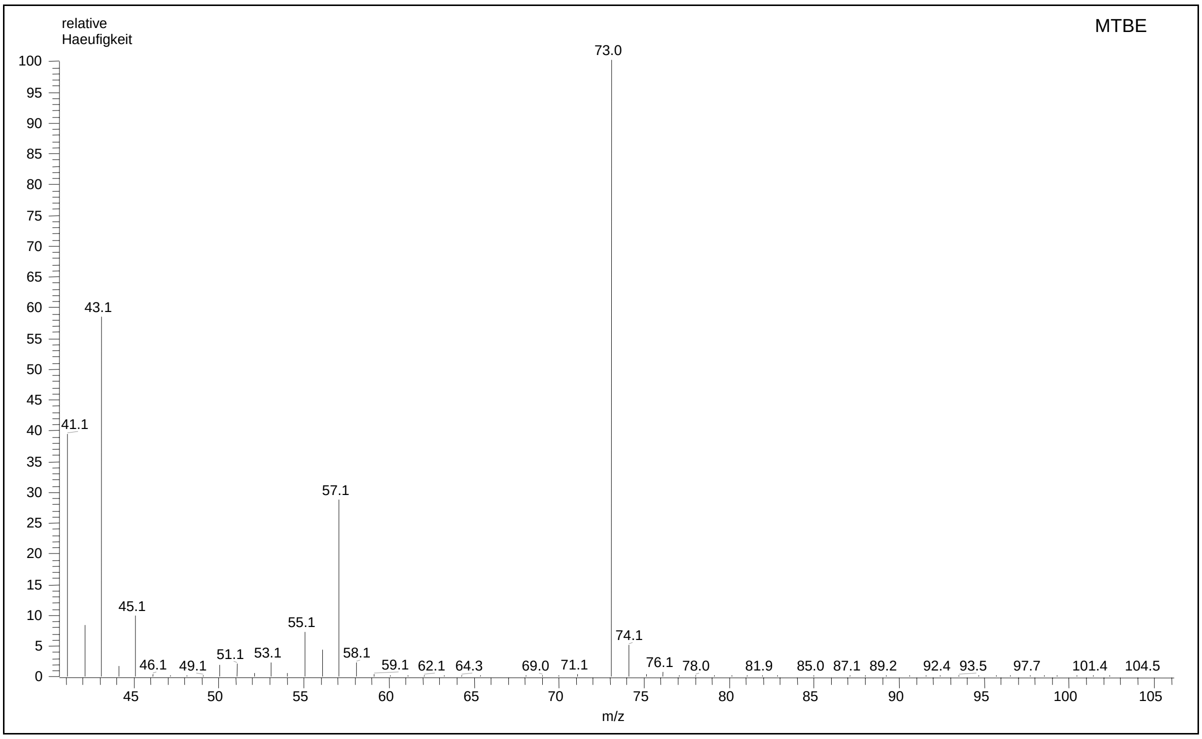

Figure 3-3: Mass spectrum of MTBE (m/z 73, 57, 43).

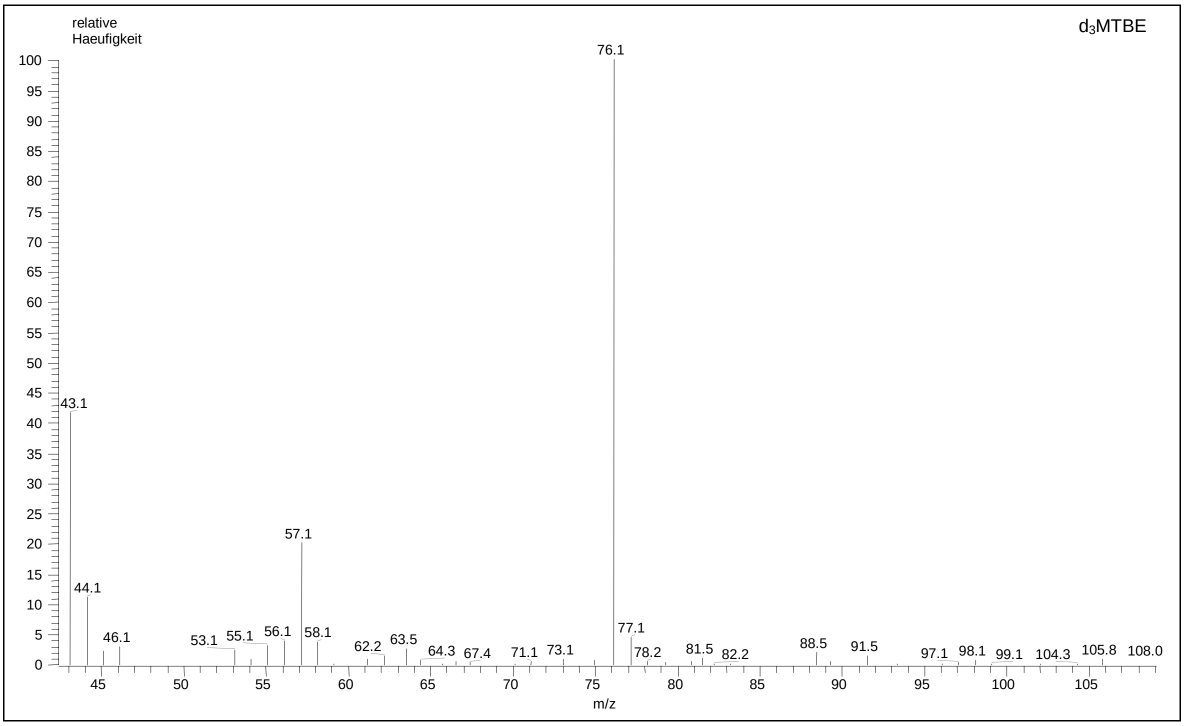

Figure 3-4: Mass spectrum of d_3MTBE (m/z 76, 57, 43).

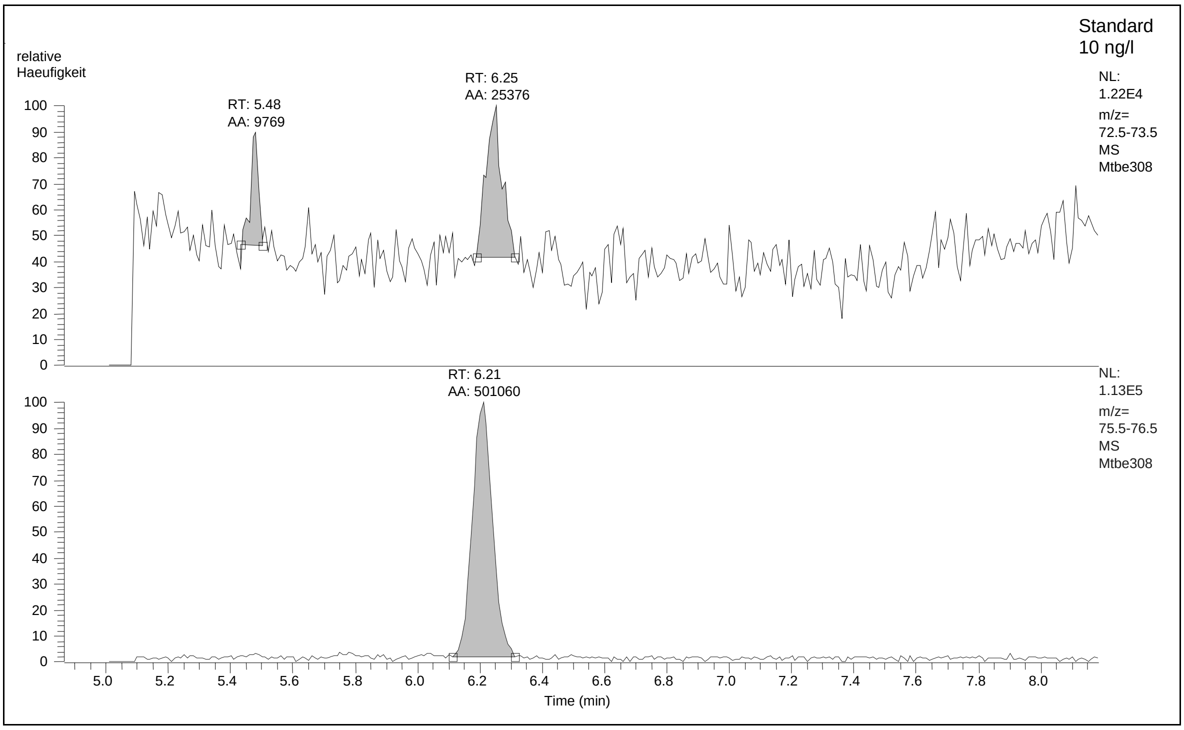

Figure 3-5: Mass chromatograms of m/z 73 (MTBE) and m/z 76 (d_3MTBE) in spiked reagent water with a MTBE concentration of 10 ng/L.

3.2.6. Calibration

Three point calibration curves (20, 100 and 5000 ng/L) (Figure 3-6) were calculated using the peak area ratios of m/z 73 and m/z 76 (internal standard d_3MTBE). The curves showed good linearity with an average correlation coefficient of R^2=0.9997. For an interlaboratory comparison study (Schumacher, *et al.*, 2003) (see also Chapter 3.1.1.), a five point calibration curve (20, 100, 200, 1000 and 5000 ng/L) was calculated, showing a linearity of R^2=0.9998 (Figure 3-7). The calibration curves were daily tested or updated by measuring calibration standards in the concentration range of the sample series, that were actually analyzed. Since MTBE could not completely be eliminated from the analytical system (Achten *et al.*, 2001c), laboratory blanks were measured every day or after the first analysis of highly contaminated samples that could not be diluted to the calibration range of 20-5000 ng/L. If the results of the blanks differed more than 10 ng/L from zero concentration, a new calibration was carried out. The quantitation of samples below 20 ng/L was carried out by updating the calibration curves with peak area ratios of m/z 73 and m/z 76 of laboratory blanks that were measured before these samples. Samples containing MTBE at concentrations higher than the calibration range were diluted.

3.2.7. Accuracy and Precision

The long-term performance (7 months) of this method investigated with spiked reagent-water concentrations of 100 ng/L revealed a recovery rate of 83-118% and a relative standard deviation (RSD) of 10%. At a concentration of 20 ng/L, the short term performance (1 day) was close to these results with a recovery rate of 96-125% and a RSD of 11% (Achten *et al.*, 2001c).

In addition to these validations, the method was further successfully prooved in the framework of an interlaboratory comparison study (Schumacher *et al.*, 2003). The determination of MTBE in the two spiked water samples (74 ng/L and 256 ng/L), that were conservated with H_2SO_4, revealed for the three point calibration (Figure 3-6) recoveries of reference values of 87% and 94% and RSDs of 16% and 9% for the 74 ng/L and 256 ng/L samples, respectively. The five point calibration (Figure 3-7) revealed recoveries of reference values of 89% and 104% and RSDs of 12% and 6%. Note that in the publication of Schumacher *et al.* (2003) only the recoveries of reference values of the five point calibration can be found.

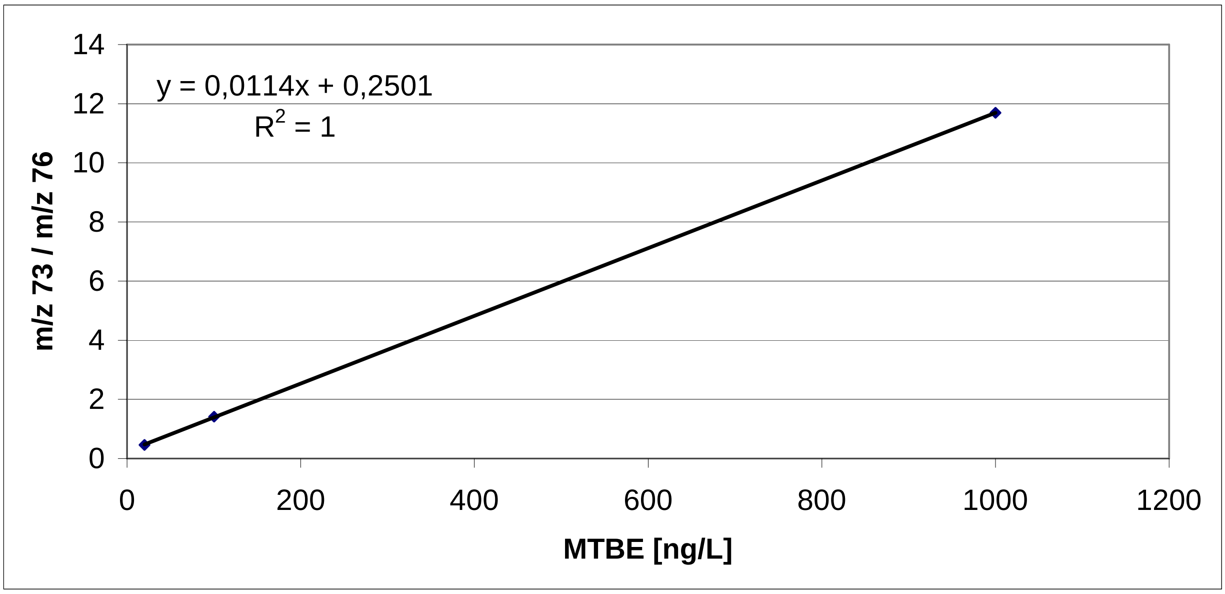

Figure 3-6: Three point calibration (20, 100, 5000 ng/L).

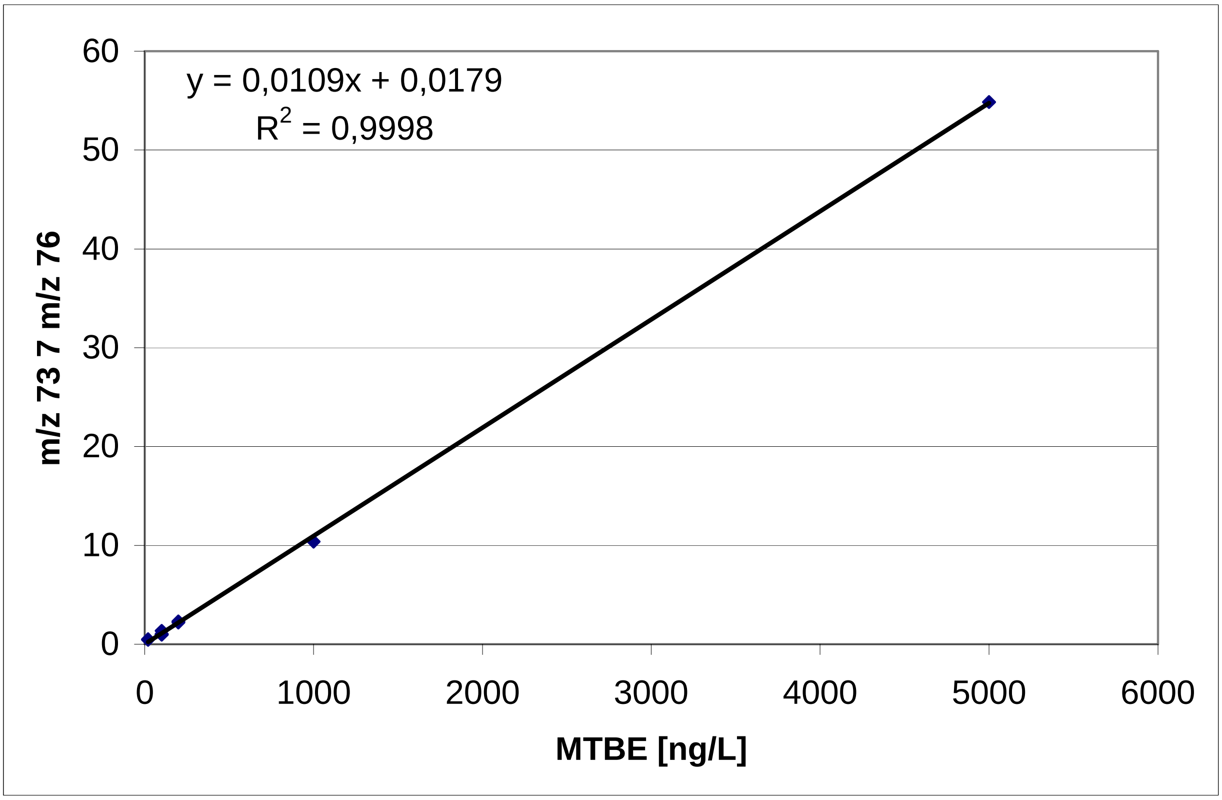

Figure 3-7: Five point calibration (20, 100, 200, 1000, 5000 ng/L).

4. MTBE IN FINISHED DRINKING WATER IN GERMANY

4.1. Abstract

In the present study 83 finished drinking water samples from 50 cities in Germany were analyzed for their methyl *tert*-butyl ether (MTBE) content by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS) with a detection limit of 10 ng/L. The detection frequency was 40% and the concentrations ranged between 17-712 ng/L, far below taste and odor thresholds or toxicological levels. The highest concentrations were found in the community water systems (CWSs) of Leuna and Spergau, these CWSs are supplied with water possibly affected by MTBE contaminated groundwater. Furthermore, MTBE could be detected at concentrations generally lower than 100 ng/L in CWSs influenced by bank filtrated water from the rivers Rhine and Main. In Frankfurt, MTBE could be found with a median concentration of 37 ng/L in all but one of 16 samples taken over a period of about 1.5 years. It can be concluded that MTBE is already present in German finished drinking water at least in certain areas. Despite the concentrations below 1 microgram per liter (µg/L), the results from Leuna and Spergau show that point sources pose the highest risk for possible MTBE contaminations in drinking water. Because of the findings in CWSs influenced by river bank filtration or artificial infiltration it can be concluded that CWSs affected by the rivers Rhine and Main are susceptible to low MTBE contaminations.

4.2. Introduction

The oxygenate methyl *tert*-butyl ether (MTBE) is added to gasoline in order to increase the octane level and to reduce carbon monoxide and hydrocarbon emissions by vehicles. MTBE is the most commonly used fuel oxygenate. In Europe, the consumption has increased by 23% between the years 1995-1999 (MEF, 2001). The annual demand of MTBE in Europe today is about 3 million tons, which equal approximately the production capacity (EFOA, 2004a). In Germany, MTBE is used mainly as an octane enhancer and therefore the concentrations in gasoline are nearly constant all year round in contrast to many parts of the United States, where it is added only seasonally. The calculated usage of MTBE as fuel additive in Germany in 2001 was 683,900 t (Sur *et al.*, 2003). Typical concentrations are 0.43%, 3.0% and 10.2% (w/w) for regular, Euro super and super premium gasoline, respectively (Sur *et al.*, 2003).

The release and distribution of MTBE in the aquatic environment has raised concern about the compound's occurrence in drinking water, due to its low taste and odor threshold and the potential impact on human health (Clawges *et al.*, 2001). In many U.S. and several European studies the detection of MTBE in stormwater (Squillace *et al.*, 1996), precipitation (Bender *et al.*, 2000; Achten *et al.*, 2001c), surface water (Reiser and O'Brien, 1998; Brauch *et al.*, 2000; Miermans *et al.*, 2000; Achten *et al.*, 2002a) and groundwater (Clawges *et al.*, 2000; Klinger *et al.*, 2002) has been reported. Sources of drinking water in the U.S. and Europe were investigated for the presence of MTBE (MEF, 2001; Delzer and Ivahnenko, 2003a). The measured concentrations were between 0.1 micrograms per liter (µg/L) and the mg/L-range, depending on the sampling, especially if the investigated water wells were affected by gasoline. An unbiased sampling was conducted in a national survey of MTBE and other VOCs in randomly selected community water systems (CWSs) in the U.S., revealing a detection frequency of 8.7% and a concentration range of 0.2-20 µg/L (Grady, 2003). Although MTBE is known to resist conventional water treatment processes (Gullick and LeChavelier, 2000; Sacher, 2002), there is, particularly in Europe, a lack of information about MTBE concentrations in finished drinking water. Single studies revealed MTBE concentrations of 80-400 ng/L and 17-110 ng/L in tap water samples in Italy and Germany, respectively (Piazza *et al.*, 2001; Sacher, 2002; Achten *et al.*, 2002b). The occurrence of MTBE in finished drinking water in the U.S. was investigated in a more representative way in a 12-state survey: After the trihalomethane compounds (total), which are often disinfectant by-products, with 41% frequency of detection, MTBE was the most frequently detected VOC. It was detectable in 8.9% of the selected 1,194 CWSs. 10 CWSs equaled or exceeded the drinking water advisory level of 20 µg/L (Grady *et al.*, 2001).

In the EU Risk Assessment Report on MTBE it is estimated that up to 50% of the European population may be exposed to MTBE via tap water at concentrations of 0.1 µg/L, if only car exhausts and rain are considered as the sources of MTBE. This would lead to a daily dose of approximately 0.2 µg/d. Tap water concentrations of up to 15 µg/L can be estimated, if underground tanks, leaks and spills at gas stations are considered as additional sources of MTBE. This would lead to a daily dose of 30 µg/d. It was not possible to determine the percentage of the population exposed to this tap water (MEF, 2001). Under consideration of economic aspects and applicability (Baus *et al.*, 2003) the removal of MTBE in waterworks is still a problem, although technologies are available for the effective and efficient removal of MTBE from municipal drinking water today (Friday *et al.*, 2001). The U.S. Environmental Protection Agency (EPA) has set its drinking water advisory level at 20-40 µg/L (USEPA, 1997). In Europe, there are currently no regulations for MTBE in drinking water, except for Denmark, which has set a limit value for MTBE in water of 30 µg/L. Other European countries are currently holding discussions to establish the guidelines and thresholds for groundwater (Schmidt *et al.*, 2001b; Sur *et al.*, 2003). MTBE levels are indeed a matter of concern for water distributors (Brauch *et al.*, 2000). One reason is a new EU guideline introduced in 2005 limiting the amount of aromatic compounds in gasoline to 35% (v/v). It is not yet clear how the required octane values will be reached after that. An increase in the consumption of fuel oxygenates is expected (Schmidt *et al.*, 2001b). This may lead to a stronger prevalence of MTBE in raw waters used for the production of drinking water.

The risk for drinking water resources to be contaminated with MTBE results mainly from point sources like leaking pipelines or leaking underground storage tanks (LUSTs), where MTBE is able to travel far distances away from the point of release with the groundwater. Higher levels of MTBE in groundwater above 20 µg/L mostly originate from point sources (USEPA, 1999). Although there is currently a lack of statistically significant relationships between storage tank density and MTBE detections in drinking water (Delzer and Ivahnenko, 2003a), gas stations (MEF, 2001; Lince *et al.*, 2001) and contaminated sites with LUSTs (Happel *et al.*, 1998) have been reported to be sources of MTBE in groundwater, which may affect drinking water sources. One example is the often cited contamination of drinking water wells in Santa Monica (Chang and Last, 1998). The large number of perhaps 250,000 MTBE-LUSTs in the immediate vicinities of community water supply wells may represent a significant threat to drinking water in the U.S. over at least the current decade (Johnson *et al.*, 2000), whereas other groups argue that the presence of MTBE does not enhance the threat that spilled or leaking gasoline poses to drinking water resources (Woodward and Sloan, 2002). The EU risk characterisation arrived to the conclusion that risks for groundwater "are mainly related to leaking underground storage tanks and spillage from overfilling the tanks" (MEF, 2001). The strict regulation of underground storage tanks (USTs) and the lower amount of MTBE in European fuel is seen by some authorities as a prevention against future problems with MTBE (Sur *et al.*, 2003). However, an increasing number of reports on point source releases that led to groundwater contamination with MTBE can be noted, but there is a lack of statistics about MTBE contaminations in groundwater caused by LUSTs (Schmidt *et al.*, 2001b).

In Germany, a few sites with MTBE contaminated groundwater have been reported (Pahlke *et al.*, 2000; Effenberger *et al.*, 2001a). One of them is located in Leuna/Saxony-Anhalt, where there is a petrochemical plant. MTBE can be detected in the groundwater with a maximum concentration of 185 mg/L and is detectable 5 km away from the source (Pahlke *et al.*, 2000). This potential source may account for possible MTBE detections in public water systems located in the vicinity.

Other possible ways for MTBE contaminations to reach drinking water supply systems represent bank filtration, a common technology in Europe (Tufenkji *et al.*, 2002), and artificial infiltration. In Germany, about 15-16% of the drinking water used is produced with the aid of such processes (Achten *et al.*, 2002b). Thus, German rivers like Rhine and Main represent a major source for drinking water. The water of these rivers was shown to contain MTBE at mean concentrations of about 0.2 µg/L and maximum concentrations of 2-10 µg/L, due to different point and nonpoint sources (Achten *et al.*, 2002a, Sacher, 2002). MTBE could be found in raw water of waterworks along these rivers, since river bank filtration as the first step in the cleanup process of waterworks does not completely eliminate MTBE (Brauch *et al.*, 2000; Achten *et al.*, 2002b).

The objective of the present study was to determine if MTBE is already present in German finished drinking water. 83 samples from 50 CWSs in Germany were analyzed for their MTBE content. The results were set in relation to additional information on the raw water of the sampled CWSs, i.e. wether the analyzed water might have been influenced by the known groundwater contamination at the Leuna site or wether the analyzed water originated from surface water via river bank filtration or artificial infiltration.

4.3. Experimental Section

4.3.1. Community Water Systems (CWSs)

The samples (Figure 4-1) were taken from 11/16/00 to 07/09/03 (Table 4-1). 11 samples originated from CWSs in Saxony-Anhalt (Hohenmölsen-Halle) in the region between Hohenmölsen, Naumburg and Halle. Two samples (Leuna and Spergau) were taken from CWSs supposed to be affected by the contaminated site, which is directly adjacent to the petrochemical plant in Leuna. At this site, MTBE concentrations above 10 mg/L were measured in groundwater downgradient towards a waterworks (UBA, 2003), which provides drinking water for Leuna (City of Leuna, 2003) and Spergau (ZWA, 2003). The waterworks is affected by the contaminated groundwater and measures of protection were already initiated (UBA, 2003). The other CWSs in Saxony-Anhalt were sampled to get a more comprehensive view.

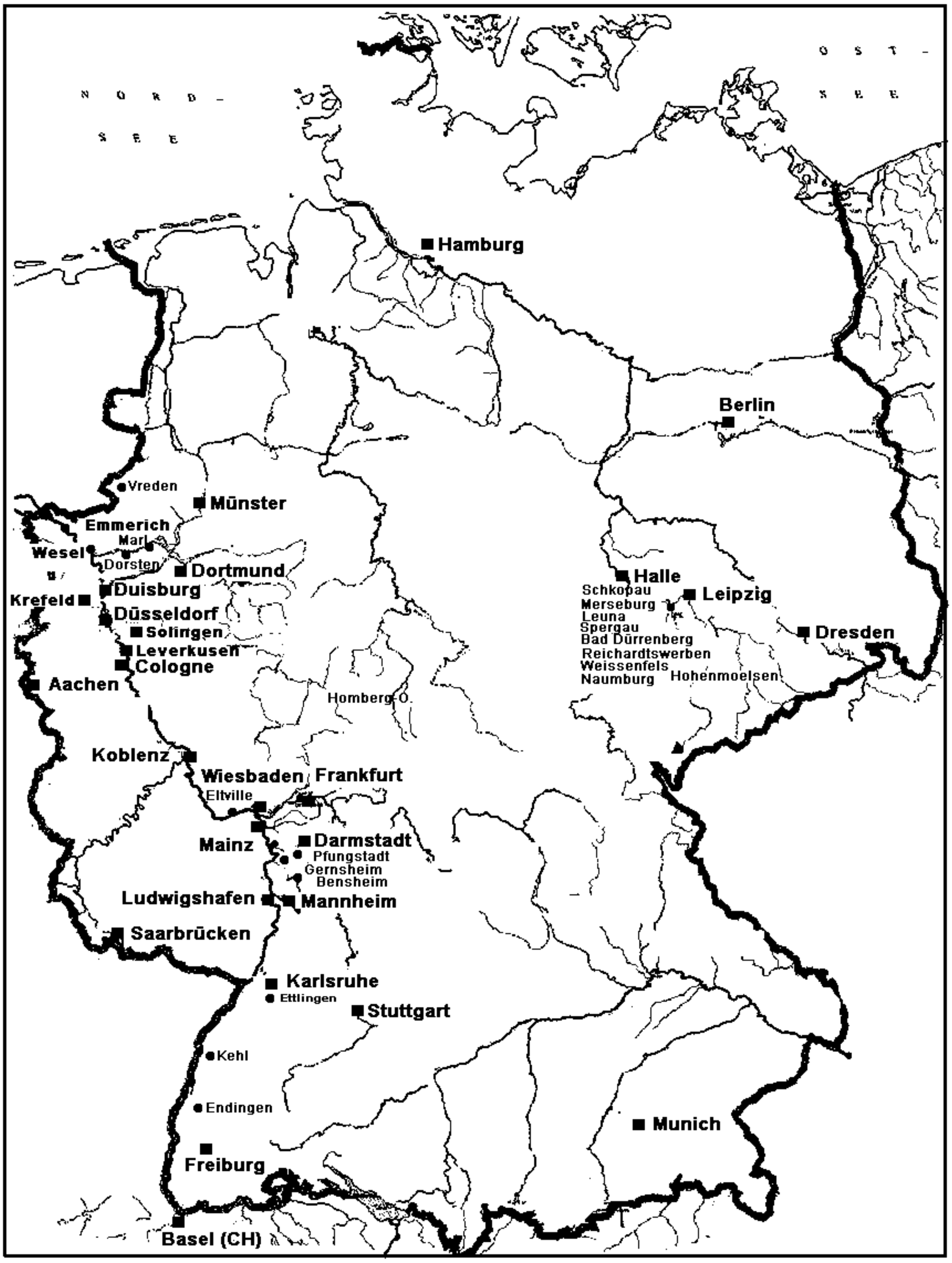

Figure 4-1: Sampled CWSs in Germany (11/16/00 to 07/09/03).

Along the river Rhine, samples from CWSs from Basel (Switzerland) to Emmerich, close to the border to The Netherlands, were taken to investigate possible influences of bank or artificially infiltrated Rhine water on the occurrence of MTBE in finished drinking water. The sampling included the CWSs of the cities Pfungstadt and Bensheim, which are not directly situated at the river Rhine, but the CWSs are probably provided with water from the drinking water area "Hessisches Ried". Water from the river Rhine is artificially infiltrated into the subsurface by plants of the local water association (Grundwasser Online, 2003) to artificially increase the water level in this important drinking water area. This association also provides drinking water for remote cities like Eltville, Wiesbaden and Frankfurt.

The CWS in Frankfurt was sampled between 11/16/00 and 06/06/02 in order to investigate the temporal behavior of MTBE occurrence in the finished drinking water. Additional samples were taken from CWSs all over Germany including big cities (Berlin-Darmstadt) as well as small cities in rural or remote areas (Endingen-Marl). Information about the sampled CWSs, especially if drinking water is provided from surface water sources by bank or artificial infiltration, was collected using available information provided by the corresponding waterworks authorities. The study included 20 CWSs with both surface and groundwater sources. The ground/surface water ratios in the samples were difficult to determine due to fluctuations and could only be estimated from the available information of the water providers. Additionally there are some CWSs containing drinking water from different origins or with different surface to groundwater ratios in different sections of the CWS in the city. The CWSs in Stuttgart, for example, provide drinking water originating from Lake Constance as well as from the Donauried region to the different city districts.

4.3.2. Sampling and Analysis

All samples were taken from taps in private households or public buildings connected to the local CWSs. The samples were stored in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. They were stored and transported at 4°C and analyzed within three weeks. During sampling and transport always field blanks were present and analyzed parallel to the samples. The analysis was performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS). Due to the origin of the samples, no high levels of monoaromatic compounds could be observed, which means that they could not limit the use of SPME (Black and Fine, 2001). Mass chromatography of m/z 73 (MTBE) and m/z 76 (internal standard d_3MTBE) was used for quantitation. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. The detection limit was 10 ng/L with a relative standard deviation of 11 %. Laboratory blanks were regularly measured. A detailed description of the analytical method is published elsewhere (Achten *et al.*, 2001b), except that a J&W Scientific DB-624 column (60 m x 0,32 mm) with a film thickness of 1.8 µm was used as chromatographic column.

4.4. Results

83 drinking water samples from CWSs supplying 50 cities were analyzed for MTBE at a detection limit of 10 ng/L (Table 4-1). MTBE was detectable in 38 samples with concentrations ranging from 17 to 712 ng/L. The detection frequency was 40 %, which means that MTBE was detected in 20 of the 50 sampled CWSs. The median (mean) concentration calculated without samples below the detection limit was 38 ng/L (89 ng/L).

The drinking water samples from Saxony-Anhalt showed a detection frequency of 60 % and a median concentration of 112 ng/L with a range of 63-712 ng/L. Maximum MTBE concentrations were measured in the samples from Leuna and Spergau. The two samples from Hohenmölsen (06/13/02 and 11/19/02) showed similar MTBE contents of 140 and 112 ng/L.

The measured MTBE concentrations in drinking water from cities located along the course of the river Rhine are shown in Figure 4-2. The CWSs which are supplied in part by bank filtrated or artificially infiltrated Rhine water are marked. In the stretch from Basel to Gernsheim, MTBE could be detected only in the samples from Basel, Karlsruhe and Mannheim, with concentrations of 17, 22 and 17 ng/L respectively. In Basel, the groundwater used to provide drinking water contains artificially infiltrated Rhine water. The waterworks providing drinking water for the cities of Karlsruhe and Mannheim do not use artificially or bank filtrated Rhine water and there is a lack of information about the drinking water in Bensheim, Pfungstadt and Gernsheim. In the region from Mainz to Emmerich MTBE was detectable in all but two (Krefeld and Wesel) drinking water samples. The concentrations ranged from 15 ng/L in Duisburg to 582 ng/L in Emmerich. The sample from Emmerich had the highest MTBE concentration of all samples taken at the Rhine cities. In the remaining CWSs with positive MTBE detections between Mainz and Emmerich, the MTBE concentrations were below 100 ng/L. The drinking water of Mainz, Wiesbaden, Cologne, Düsseldorf and Duisburg is at least partly composed of groundwater affected by Rhine water. The cities of Leverkusen, Krefeld and Wesel do not use Rhine-influenced raw water; detailed information about the origin of the drinking water provided for the CWSs in Eltville, Koblenz and Emmerich was not available. MTBE was detected in 55 % of the CWSs located at the river Rhine that were sampled for MTBE. The median (mean) value was 36 ng/L (69 ng/L).

City (CWS)/Federal State	**sampling date**	**No. of samples**	**MTBE [ng/l]**	**CWS - source of water [gw, sw: bf,ai,b] (%)(sw body)**
Hohenmölsen / Saxony-Anhalt	06/13/02-11/19/02	2	112 - 140	n.i.
Naumburg / Saxony-Anhalt	11/18/02	1	<10	gw, sw: bf (~100%) (Saale)
Weissenfels / Saxony-Anhalt	11/18/02	1	<10	n.i.
Reichardtswerben / Saxony-Anhalt	11/19/02	1	<10	n.i.
Bad Duerrenberg / Saxony-Anhalt	11/18/02	1	76	sw: b (Rappbodetalsperre)
Spergau / Saxony-Anhalt	11/18/02	1	608	gw, waterworks in vicinity to contaminated site
Leuna / Saxony-Anhalt	11/18/02	1	712	gw, waterworks in vicinity to contaminated site
Merseburg / Saxony-Anhalt	11/18/02	1	76	gw, sw: bf (Elbe), b (Rappbodetalsperre)
Schkopau / Saxony-Anhalt	11/19/02	1	63	n.i.
Halle / Saxony-Anhalt	11/19/02	1	<10	n.i.
Basel (CH)	05/24/03	1	17	gw, sw: ai (50-70%) (Rhine)
Kehl / Baden-Württemberg	10/18/02	1	<10	gw
Ettlingen / Baden-Württemberg	05/27/03	1	<10	gw
Karlsruhe / Baden-Württemberg	06/10/02-05/27/03	4	<10 - 31	gw
Mannheim / Baden Württemberg	06/10/02-05/27/03	3	<10 - 17	gw
Ludwigshafen / Rhineland-Palatinate	10/18/02	1	<10	gw
Bensheim / Hesse	10/25/02	1	<10	n.i.
Pfungstadt / Hesse	10/25/02	1	<10	n.i.
Gernsheim / Hesse	05/27/03	1	<10	n.i.
Mainz / Rhineland-Palatinate	10/18/02-05/21/03	2	43	gw, sw: bf (Rhine)
Wiesbaden / Hesse	06/07/02	1	34	gw, sw: bf (Rhine)
Eltville / Hesse	06/10/02	1	38	gw, n.i.
Koblenz / Rhineland-Palatinate	07/09/03	1	71	n.i.
Cologne / North Rhine-Westphalia	06/23/01	2	53 - 56	gw, sw: bf (0-60%)(Rhine)
Leverkusen / North Rhine-Westphalia	11/27/02	1	31	gw
Düsseldorf / North Rhine-Westphalia	10/12/02-05/07/03	3	25 - 48	gw, sw: ai (75%), bf (Rhine)
Krefeld / North Rhine-Westphalia	05/07/03	1	<10	gw
Duisburg / North Rhine-Westphalia	05/07/03	2	<10 - 15	gw, sw: bf (~40%) (Rhine)
Wesel / North Rhine-Westphalia	05/08/03	1	<10	gw
Emmerich / North Rhine-Westphalia	05/07/03	1	582	n.i.
Frankfurt / Hesse*	11/16/00-06/06/02	16	<10 - 96	gw, sw: bf (Main), ai (Rhine)
Berlin	08/24/02	2	<10 - 17	gw, sw: bf (57%), ai (13%)
Hamburg	05/23/03	2	<10	gw
Munich / Bavaria	07/01/02	2	<10	gw
Dortmund / North Rhine-Westphalia	08/07/02	1	<10	gw, sw: ai, bf (mostly < 10%) (Ruhr)
Stuttgart / Baden-Württemberg	06/27/02	1	<10	gw, sw (Lake Constance)
Leipzig / Saxony	08/20/02	2	<10	gw, sw: bf (5-100%) (Mulde, Parthe)
Dresden / Saxony	07/25/02	1	<10	gw, sw: bf (20-25%) (Elbe)
Muenster / North Rhine-Westphalia	06/14/02	1	<10	gw, sw: ai
Aachen / North Rhine-Westphalia	06/09/02	2	<10	gw, sw: b (~70%, Ruhr, Urft, Olef, Wehebach)
Freiburg / Baden-Württemberg	10/31/02	1	<10	gw
Saarbruecken / Saar	07/08/02	1	<10	n.i.
Solingen / North Rhine-Westphalia	06/16/02	1	<10	gw,sw (80%)
Darmstadt / Hesse	06/20/02	1	<10	n.i.
Endingen a.K./ Baden-Württemberg	06/03/02	1	<10	gw
Homberg-O. / Hesse	08/15/02	2	<10	gw
Vreden / North Rhine-Westphalia	06/16/02	1	<10	n.i.
Dorsten / North Rhine-Westphalia	05/08/03	1	<10	gw
Haltern / North Rhine-Westphalia	05/08/03	1	<10	gw, sw: bf, ai
Marl / North Rhine-Westphalia	05/08/03	2	<10	gw, sw: bf, ai

*Table 4-1: Sampled CWSs; source of water: groundwater (gw), surface water (sw): bank filtration (bf), artificial infiltration (ai), barrier (b); if available percentages and name of the surface water body; no information (n.i.). *data from 13 samples of Frankfurt/Main were already published (Achten et al., 2002b). For single results see Appendix Table A1.*

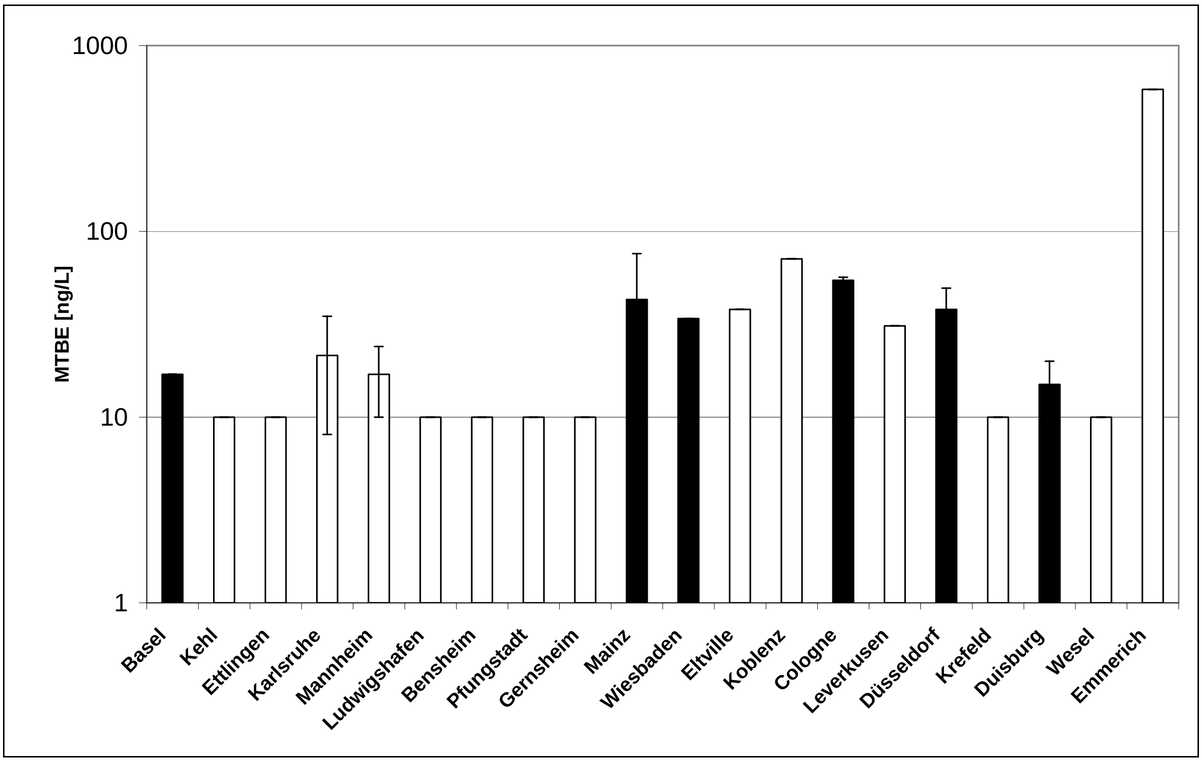

Figure 4-2: MTBE concentrations (logarithmic scale) in water from CWSs at the river Rhine; CWSs using bank filtrated Rhine water are shown in black. Method detection limit was 10 ng/L with a relative standard deviation of 11%. If more than one sample from the related CWS was taken, mean values with standard deviations are represented. For single results see Appendix Table A1.

MTBE was detected only in 2 (namely Frankfurt and Berlin) of 20 CWSs located in regions other than Saxony-Anhalt and along the course of the river Rhine. In the case of Berlin, where the drinking water is also influenced by bank filtrated river water, MTBE was found in the drinking water with a concentration of 17 ng/L. Figure 4-3 shows the temporal variability of MTBE concentrations in drinking water samples from the CWS in Frankfurt. The median (mean) concentration was 37 ng/L (41 ng/L) with a concentration range of 17-96 ng/L. Only in one sample (11/25/00) the concentration of MTBE was below the detection limit. The drinking water in Frankfurt is influenced by artificially infiltrated water from the rivers Rhine and Main. In comparison to the 10 samples from CWSs in Saxony-Anhalt, the sampling along the river Rhine and the remaining cities consisted in each case of 20 different CWSs. Compared to the drinking water samples from the cities at the river Rhine and the remaining samples, the samples from Saxony-Anhalt showed the highest overall MTBE concentrations with 712 ng/L and 608 ng/L in the samples from Leuna and Spergau, respectively. Only five samples were measured at concentrations above 100 ng/L. Four of them originated from CWSs in Saxony-Anhalt and one was taken from the CWSs in Emmerich at the river Rhine. The median MTBE concentration (112 ng/L) of the drinking water samples from Saxony-Anhalt was about three times above the median concentration of 36 and 35 ng/L in the CWSs along the river Rhine and the remaining samples, respectively. The detection frequencies of MTBE in finished drinking water were about six times higher in the sampled CWSs in Saxony-Anhalt (60%) and along the river Rhine (55%) than in the remaining CWSs (10%) including Frankfurt.

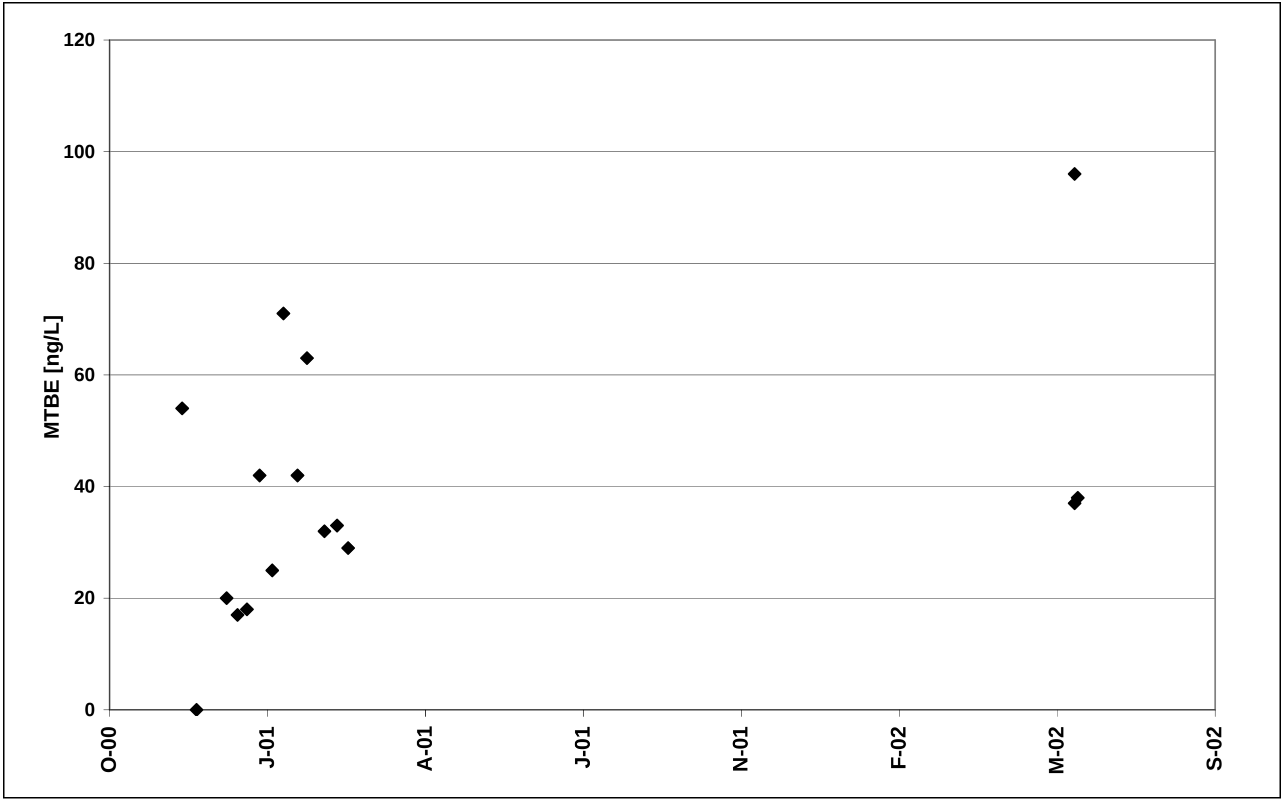

Figure 4-3: MTBE concentrations in samples from the CWS in Frankfurt. Method detection limit was 10 ng/L with a relative standard deviation of 11%. For single results see Appendix Table A1.

4.5. Discussion

The MTBE concentrations in finished drinking water in Germany measured in this study were generally about one order of magnitude below the USEPA drinking water advisory of 20-40 μg/L. However, the data obtained indicate that the probability to detect MTBE in drinking water in Germany is dependent on the area and the source of water which is used to provide drinking water. Although detection frequencies were determined during the evaluation, the low and statistically not representative sample amount has to be kept in mind, which also limits the association of MTBE detections with ancillary information like population density or land use. Above all, in the U.S., population density seems to correlate positively with volatile organic compound (VOC) detections in ambient ground water (Squillace *et al.*, 1999) and MTBE detections in water supplies (Delzer and Ivahnenko, 2003a), drinking water sources (Grady, 2003) and finished drinking water (Grady and Casey, 2001). Another important ancillary factor for MTBE detections in groundwater (Squillace *et al.*, 1999; Moran *et al.*, 1999) and drinking water (Grady and Casey, 2001; Grady, 2003) in the U.S. is the amount of MTBE use in different areas. In Germany, no area specific MTBE amounts are added to gasoline and about the same average concentrations are used throughout the year. Therefore, the occurrence of MTBE in drinking water in the different study areas within this study cannot be associated with different MTBE use patterns. In addition to these ancillary factors, site-specific conditions like contaminations or river bank and artificial infiltration seem to be more important to explain at least in part some of the findings of this study. The biased sampling and the low detection limit of 10 ng/L may explain the detection frequency of 40% compared to 8.9% at any reporting level in the U.S. 12-state survey (Grady and Casey, 2001). For the same reasons it is difficult to statistically compare the 12-state survey and the present study.

The maximum detection frequency could be observed in the samples from Saxony-Anhalt, and the highest concentrations were measured in Leuna and Spergau. These cities are only a few kilometers away from the known groundwater contamination in Leuna. Although it was not possible within the scope of this study to test the topographic or hydrogeological relationship between the contaminated site and the local CWSs, the contaminated groundwater most probably accounts for MTBE detections in the CWSs of Leuna and Spergau. The concentrations measured in Leuna and Spergau are about 8 times lower than the California 5 µg/L taste and odor level and far below toxic concentrations (Sur *et al.*, 2003). Nevertheless, these findings may reflect the threat posed by past MTBE releases on community water supply wells as described by Johnson *et al.* (2000). At the Leuna petrochemical plant, 50,000 t of MTBE are produced (Pahlke *et al.*, 2000) so that the latter's occurrence in drinking water may reflect the increased background concentration in this area. The MTBE concentrations above 100 ng/L in the drinking water samples from Hohenmölsen and the MTBE detections in the remaining samples from Saxony-Anhalt remain unclear. There might be point sources like gas stations with LUSTs or industrial plants with releases of MTBE into the subsurface.

30 samples from 20 CWSs located along the river Rhine have been analyzed for MTBE, showing a detection frequency of 55%. Sampling from cities at the upper part of the river Rhine (Basel-Gernsheim) resulted in a detection frequency of 33%. MTBE was more detectable in CWSs of cities at the lower part of the river Rhine (Mainz-Emmerich) with a detection frequency of 82%. This might be due to ancillary factors like population and industrial density. A similar pattern was obtained in a study where river water spot sampling at the river Rhine was performed during two days (Achten *et al.*, 2002a). Certainly, the similarity between MTBE concentrations in the river Rhine and the drinking water from CWSs located close to the river is only possible if the investigated drinking water originates substantially from infiltrated or treated river water. On the basis of the available information, these conditions are met in six of the sampled CWSs along the Rhine. And in all six of them MTBE could be found in detectable amounts. The determination of the different ratios of groundwater to river water which could be found in the drinking water samples could be estimated only roughly and the sample amount was too low to associate them quantitatively with the MTBE concentrations found. Nevertheless, it seems likely that MTBE concentrations in drinking water are higher the more bank filtrated Rhine water is used for drinking water. These findings are supported by the results of studies on the occurrence and behavior of MTBE during bank filtration (Brauch *et al.*, 2000; Sacher, 2002; Achten *et al.*, 2002b) and raw water cleanup technologies in waterworks (Baus *et al.*, 2003). The results showed that during the bank filtration process MTBE was never completely eliminated. The compound was evaluated as a “compound of relevance for waterworks” (Brauch *et al.*, 2000). Reduced amounts of MTBE in bank filtrated water may be due to degradation and adsorption processes but also to dilution by groundwater within the aquifer (Sacher, 2002). MTBE concentrations of about 50-180 ng/L measured in raw water during the mentioned studies were about 40-50% of the MTBE concentrations measured in the corresponding river Rhine. The concentrations in finished drinking water samples were approximately 43-110 ng/L and comparable to the median values in this study of 36 and 35 ng/L for the CWSs at the river Rhine and in Frankfurt respectively.

Apart from the Leuna area and the river Rhine, MTBE was only hardly detectable, with the exception of Frankfurt, where MTBE was found in all but one sample over a period of about two years. Drinking water in Frankfurt is influenced by Rhine and Main water, using artificial infiltration and bank filtration, respectively. Similar to the river Rhine, MTBE is detectable in the lower Main at concentrations of about 200 ng/L (Püttmann *et al.*, 2002). Therefore, as well as in CWSs at the river Rhine, the pathway of MTBE from the river into waterworks and the provided drinking water is presumably similar.

If the Frankfurt samples are neglected, MTBE was only detectable in one CWSs in the remaining samples with a concentration of 17 ng/L in Berlin, where drinking water also originates in part from bank filtrated water, but no information about the occurrence of MTBE in the corresponding surface water was available. The CWSs where MTBE could not be detected within this study provide water to large cities like Stuttgart, Leipzig and Aachen. Some of the drinking water samples of the remaining CWSs are also influenced by surface water, but the lakes (e.g. for Stuttgart), rivers (e.g. for Leipzig), or reservoirs (e.g. for Aachen) are rural or might not be affected by MTBE like the rivers Rhine and Main.

The occurrence of MTBE in some large CWSs influenced by surface water sources is in accordance to observations in U.S. studies. In the random national survey of MTBE and other VOCs in drinking water sources, MTBE was significantly more detectable in surface water sources (14%) than in groundwater sources (5.4%) and generally more detectable in large CWSs independent of the type of source waters (Grady, 2003). The median concentrations of groundwater (710 ng/L) and reservoir samples (670 ng/L) were significantly higher than those of river samples (320 ng/L), maybe because of more efficient mixing and diluting processes in flowing water or less motorized watercraft use in the selected rivers (Grady, 2003). The associated focused survey with a detection frequency of 55% in selected sources of drinking water revealed a weak seasonal pattern in samples collected from reservoirs and lakes, which might be due to seasonal patterns in the use of motorized watercraft. Seasonal differences in river and stream source waters could not be observed. This probably indicated a common and continuous source of contamination (Delzer and Ivahnenko, 2003b). In Germany, several sources of MTBE in river water have been described and median concentrations in the rivers Rhine and Main are approximately 200 ng/L, but maximum concentrations can increase up to 10 µg/L (Achten *et al.*, 2002a; Sacher, 2002). Within the 12-state survey of MTBE and other VOCs in finished drinking water in the U.S., MTBE was at or above 1 µg/L more often detectable in CWSs supplied only by groundwater sources (7.8 %) than in those supplied only by surface water sources (2.6 %). In large CWSs using both sources the detection frequency was highest (16 %). The survey presumed that this reflects the situation at larger systems in urban areas. The combination of surface and groundwater sources together with the association of MTBE with urban sources may be responsible for these higher detection frequencies (Grady and Casey, 2001). This may also explain the MTBE detection in the CWSs located at the Rhine, in Frankfurt and in Berlin. On the basis of the present study and the available information about the CWSs, the river Rhine seems to be a major source for MTBE in finished drinking water, since MTBE occurred in all of the sampled CWSs influenced by Rhine water through bank or artificial filtration.

In addition to the possible different pathways for MTBE to reach drinking water supplies, the frequent detections of MTBE at least among certain samples raise the question of how to deal with MTBE contaminations in waterworks. Regardless of the sources and the generally low concentrations measured in this study, MTBE poses a risk for drinking water, since drinking water seems to be contaminated to a greater extent from gasoline containing MTBE (Grady and Casey, 2001). A lot of work has been done and will continue in the future in terms of MTBE remediation technologies, e.g. at the contaminated Leuna site (Martienssen and Schirmer, 2003). Some common "myths", primarily that MTBE cannot be remediated, appear to be disproved indeed (Woodward and Sloan, 2002) and there are promising technologies to treat MTBE-contaminated water (California MTBE Research Partnership, 1999; Anderson, 2000; Stefan *et al.*, 2000; Effenberger *et al.*, 2001b; Woodward and Sloan, 2002, Leethem, 2002). However, for waterworks the applicability of established or advanced processes to remove MTBE even at low concentrations and the cost efficiency is important. The efficiency of MTBE removal during drinking water treatment with technologies like aeration, activated carbon and advanced oxidation processes, that are commonly used in Germany was investigated in laboratory-scale experiments (Baus *et al.*, 2003). The latter's results as well as the positive MTBE detections of the present study indicate that the current cleanup technologies used in German waterworks are able to eliminate MTBE, but only with expensive modifications. On the other hand, all concentrations measured in finished drinking water in Germany were below 1 µg/L and about one order of magnitude below the USEPA drinking water advisory level of 20-40 µg/L. Generally low MTBE concentrations in finished drinking water also appeared during the U.S. 12-state survey, since about 40% of the CWSs with MTBE detections had median concentrations less than 1 µg/L and only 0.8% of the selected 1,194 CWSs equaled or exceeded the 20 µg/L level (Grady and Casey, 2001). To which extent possible MTBE contaminations in waterworks should be eliminated will be determined by taste and odor thresholds, rather than by toxicological criteria. Toxicological effects were observed in animal studies during oral exposition (MAK, 2000) orders of magnitude higher than organoleptic/odor thresholds (USEPA, 1997; Sur *et al.*, 2003). A scientifically supported odor value, for example, is 15 µg/L (Stocking *et al.*, 2001). These findings also support the result of the EU risk characterisation that "there is a need for limiting the risks due to the potability of drinking water" and the maximum MTBE concentration in drinking water of 15 µg/L for a reasonable worst case scenario (MEF, 2001). The increase of MTBE usage in Germany following the new EU guideline was recently estimated to be insignificant due to already low amounts of aromatic compounds in German gasoline (Sur *et al.*, 2003).

Nevertheless, it can be concluded that MTBE is not eliminated by the current drinking water processing technologies. Moreover, in light of the detected MTBE contamination in drinking water from the area of Leuna with a known groundwater contamination, the question arises whether further locations exist in Germany with similar interrelationships. Routine monitoring programs are required in Germany to investigate the possible influence of further MTBE-contaminated sites on the drinking water quality in surrounding areas. The results from the sampling at CWSs at the river Rhine and in Frankfurt show that CWSs supplied by river bank filtration are susceptible at least to low MTBE contaminations. Efforts to avoid MTBE contamination eliminate the need for MTBE remediation. The unique physical-chemical properties of MTBE compared to other fuel constituents may classify the use of MTBE only as an “intermediate state in terms of precaution” (Sur *et al.*, 2003). Currently, some petroleum companies are proposing the substitution of MTBE by ethyl *tert*-butyl ether (ETBE) (Shell, 2004) in order to address the EU requirement to increase the addition of biofuel to gasoline (Sur *et al.*, 2003). Thereby, the ethyl component of ETBE would originate from the reaction of bioethanol with isobutene. In terms of environmental aspects the advantage of ETBE over MTBE is not yet proven with respect to their behavior in groundwater.

5. INFLUENCE OF POSSIBLE MTBE SOURCES ON THE SPATIAL MTBE DISTRIBUTION IN THREE GERMAN RIVERS

5.1. Abstract

The investigation of the spatial distribution of MTBE in three German rivers and a canal with potential emission sources located close to the course of the rivers revealed median MTBE concentrations in the range of 133-368 ng/L. At the river Lippe between Datteln and Wesel, the potential influence of discharges by a chemical park including an MTBE producing plant was only weakly observable. The parallel flowing Wesel-Datteln-Canal receives MTBE emissions most probably through boating traffic. The analyses of samples taken at the river Saale between Naumburg and Halle and at the river Rhine near Karlsruhe revealed MTBE emissions, which can be regarded as point sources. A known groundwater contamination, where the Saale is the receiving stream, is most probably the source for a noticeable raise of the MTBE concentrations from 24 ng/L to 379 ng/L. Increasing MTBE concentrations from 73 ng/L up to 5 micrograms per liter (µg/L) could be observed in the river Rhine near Karlsruhe. The detected MTBE most probably originates from the local refinery/tank farm area. The measured surface water concentrations were in the lower range of predicted environmental concentrations (PECs) calculated in the EU risk assessment for MTBE. It can be concluded that the difference between previous calculations using the equilibrium criterion (EQC) model (19 ng/L) and measured average MTBE concentrations in German surface water (50 ng/L) may be explained at least partly by additional possible emission sources like contaminated groundwater and tank farms. The contribution of leaking loading/unloading harbor facilities and motorized watercraft to the aqueous emission rate of MTBE in Germany yet also may have been underestimated.

5.2. Introduction

The oxygenate methyl *tert*-butyl ether (MTBE) is mainly used as fuel additive to reduce air pollution. The annual demand of MTBE in Europe today is about 3 million tons and approximately equal to the production capacity (EFOA, 2004a). The calculated amount of MTBE used as fuel additive in Germany for the year 2001 was 683,900 t (Sur *et al.*, 2003). Its occurrence in the aquatic environment (Squillace *et al.*, 1996; Reiser and O’Brien, 1998; Bender *et al.*, 2000; MEF, 2001; Clawges *et al.*, 2000; Brauch, 2000; Miermans *et al.*, 2000; Achten *et al.*, 2001c; Effenberger *et al.*, 2001a; Klinger *et al.*, 2002; Achten *et al.*, 2002a) has led to concern in the USA and Europe because of its potential threat for drinking water sources (Clawges *et al.*, 2001; MEF, 2001; Grady, 2003). MTBE has a low taste and odor threshold of 5-40 micrograms per liter (µg/L) (USEPA, 1997; Jacobs, 2001; Stocking *et al.*, 2001) as well as physico-chemical properties that enable it to migrate long distances within the groundwater at almost the same velocities as those of the recharge water (Squillace *et al.*, 1996). Beside groundwater, surface water represents a source for drinking water, since bank filtration is a common technology in Europe (Tufenkji *et al.*, 2002) and about 15-16% of the drinking water used in Germany is produced via bank or artificial infiltration (Achten *et al.*, 2002b). Recent studies indicated the persistence of MTBE during bank filtration and treatment processes in waterworks. Bank filtrated water and finished drinking water in Germany were shown to contain MTBE in detectable amounts, but only one order of magnitude below the known taste and odor thresholds (Achten *et al.*, 2002b; Sacher, 2002). Despite the low concentrations in drinking water, information on the behavior, occurrence and sources of MTBE in European surface water is important for precautionary reasons. MTBE has been described to be potentially degradable in water under aerobic conditions (Bradley *et al.*, 2001b) and it was shown to be degradable in sediments under aerobic and anaerobic conditions (Bradley *et al.*, 1999, 2001a, 2001b). MTBE volatilization from rivers and streams depends on ambient conditions. The travel distance in streams ranges from 0.8 km to 900 km before half of the MTBE is volatilized (Pankow *et al.*, 1996).

MTBE is emitted through a number of sources into surface water. A diffusive source is precipitation and urban runoff (Bender *et al.*, 2000; Achten *et al.*, 2001c), important mainly for small rural streams without input of industrial/domestic wastewater (Achten *et al.*, 2002a). Nevertheless, this source should not be neglected, since emissions to air from the use of gasoline have been proposed to be the main source of MTBE releases to the environment (MEF, 2001). Less diffusive and more punctual sources to surface water are industrial and community sewage treatment plants containing urban runoff, gasoline-fueled watercraft, losses of MTBE during shipping transport and MTBE contaminated groundwater. Industrial discharges at sites, where great amounts of MTBE are produced, used or stored, may be seen as point sources. The EU risk assessment for MTBE (MEF, 2001) contains generic and site-specific predicted environmental concentrations (PECs) in surface water including MTBE production, formulation, storage and processing sites as well as motorized water boating and stormwater runoff. Within the EU, there are 29 production and/or formulation sites. The calculated regional and continental PECs of 1.5

μg/L and 0.1 μg/L are in reasonable good agreement with monitoring data (Miermans *et al.*, 2000; MEF, 2001; Püttmann *et al.*, 2002). Maximum MTBE concentrations of up to about 50 μg/L and more close to the calculated local PECs in industrially or motorized watercraft influenced surface water were reported in Europe and in the U.S. (Reuter *et al.*, 1998; Dale *et al.*, 2000; Brown *et al.*, 2001; Achten *et al.*, 2002a; An *et al.*, 2002; Zuccarello *et al.*, 2003).

Compartment modelling and estimations of aquatic MTBE input in Germany using the equilibrium criterion (EQC) model revealed a mean surface water concentration in Germany of 19 ng/L (Achten *et al.*, 2002c). The calculation was carried out on the assumption of an atmospheric emission rate of 2,285 tons per year (t/a) and an aqueous emission rate of 50 t/a in Germany. A rough estimation using monitoring data revealed an average MTBE concentration in German surface water (1999/2000) of 50 ng/L, more than twice as high as the calculated concentration of the EQC model. Inadequate fixed model parameters and/or an underestimation of the MTBE input from point sources into the surface water in Germany might be the reason for the observed difference. The limited amount of MTBE data from industrial effluent samples and/or unknown emission sources could explain the higher emission rate derived from monitoring data. The amount of MTBE directly emitted into surface water from point sources is a very sensitive parameter for the MTBE concentration in the aquatic environment (Achten *et al.*, 2002c).

Point sources of MTBE emission into surface water can be detected either through sampling of effluents or through detailed sampling of surface water in the area, where the possible source is located. Recently, community and industrial wastewater treatment plants have been shown to be sources for intermittent MTBE releases to river water with effluent concentrations in the range of 13 ng/L to about 3 μg/L and 14 ng/L to about 28 μg/L respectively (Kolb *et al.*, 2003). However, the spatial patterns of MTBE in receiving water may not resemble patterns that were obtained through sampling effluents, at least if the receiving water is used for recreational boating (Brown *et al.*, 2001). A possible source of MTBE in the river Rhine was detected by elevated MTBE concentrations measured in samples downstream from a chemical plant located on the left side of the river (Sacher, 2002). Elevated concentrations of 500 ng/L to 25 μg/L MTBE in the Lower Rhine were also detected by continuously monitoring automatic systems indicating intermittent MTBE releases from yet unknown sources (Gerke *et al.*, 2003).

The objective of this study is to investigate additional possible MTBE emission sources that may contribute to explain the difference between the mean surface water concentrations calculated by using the EQC model and the estimated average MTBE concentration in German surface water (Achten *et al.*, 2002c). Therefore, the spatial distribution of MTBE in three rivers was investigated in areas, where MTBE production/storage sites and known groundwater contaminations are located. Additionally, water from a canal flowing parallel to one of the rivers was sampled. The data were also compared to PECs calculated in the EU risk assessment (MEF, 2001).

5.3. Experimental Section

In order to investigate the spatial distribution of MTBE at three study sites, spot sampling within 1-2 days was performed at the river Lippe/Wesel-Datteln-Canal, two affluents of the river Rhine, at the river Saale, an affluent of the Elbe, and at the river Rhine. At the three study sites, MTBE producing plants/refineries, tank farms or known groundwater contaminations are located close to the course of the river. Generally, the samples were taken at the bank, where the potential MTBE sources are located. This means the Lippe/Wesel-Datteln-Canal and the Saale were sampled at the left bank, whereas the river Rhine in the region of Karlsruhe was sampled at the right bank.

5.3.1. Study Sites

Spot sampling was performed from 05/07/03 to 05/08/03 at the river Lippe and the Wesel-Datteln-Canal (Figure 5-1) in North Rhine-Westphalia. Between Datteln and the mouth into the river Rhine at Wesel, the Wesel-Datteln-Canal is flowing parallel to the Lippe with a length of 60 km. The Lippe is a small affluent of the river Rhine with a water flow of about 10-90 m^3/s (Ruppert and Zach, 2003). The Wesel-Datteln-Canal is regulated for shipping traffic and together with the Dortmund-Ems-Canal, the Rhine-Herne-Canal and the Datteln-Hamm-Canal part of the Western German Canal system. These canals are important waterways to connect the Rhine with other rivers such as Ems, Weser, Elbe and Oder. At Hamm, about 35 km away from Datteln, water of the river Lippe is transferred into the Datteln-Hamm-Canal to enrich the Western German Canals with water. On the other hand, the river Lippe can be fed with water from the canal system in dry periods when the water flow in the Lippe is less than 10 m^3/s, (Ruppert and Zach, 2003). In addition to its function as waterway for freight traffic, the Wesel-Datteln-Canal is also used for recreational boating; a marina, for example, is found in the city of Dorsten. At the city of Marl, at a distance of approximately 37 km to the mouth of the two streams into the river Rhine, the Marl Chemical Park is situated south of the canal. In a chemical plant located in this park, 150,000 t of MTBE are produced per year (Pahlke *et al.*, 2000). The wastewater of the chemical park is treated in two sewage plants and discharged into the Lippe (Chemiepark Marl, 2003). The park is linked to the river Rhine through harbor facilities at the Wesel-Datteln-Canal. During the sampling, 9 samples from the Lippe and 9 samples from the canal were taken. Two sites (L1, L2, WDC1, WDC2) are located upstream of the chemical park. The sampling consisted furthermore of additional sites upstream (R12, Duisburg, Krefeld, Düsseldorf) and downstream (R13, R14, Bislich, Emmerich) of the mouths at the river Rhine.

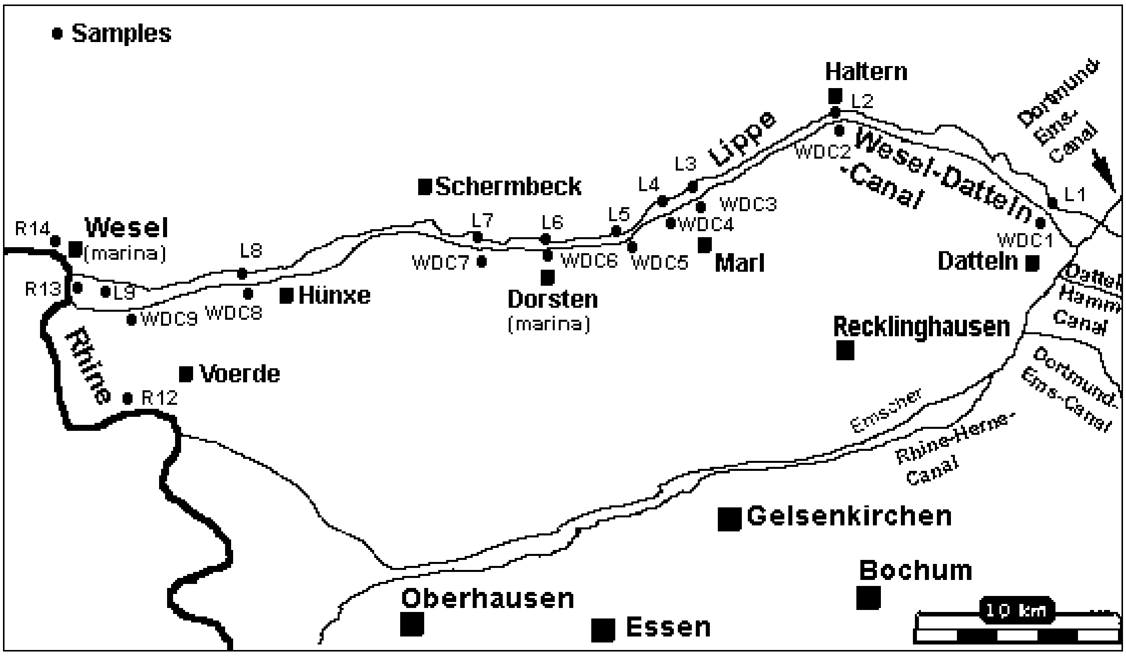

Figure 5-1: Location of sample collection from the river Lippe and the Wesel-Datteln-Canal from 05/07/03-05/08/03.

Samples from the river Saale in Saxony-Anhalt were obtained from 11/18/02-11/19/02 between Naumburg and Halle (Figure 5-2) at a distance of about 40 km. The chemical site Leuna with a petrochemical plant is situated 1-2 km west of the river, producing about 50,000 t MTBE per year (Pahlke *et al.*, 2000). Wastewater from the chemical site is directed through wastewater disposal facilities into the river Saale (Infra Leuna, 2003). Additionally, a known groundwater contamination with MTBE concentrations above 10 mg/L can be found in this area. Protective measures of the waterworks located nearby were already initiated. The river Saale is the receiving stream for the upper aquifer of the contaminated site. Before initiating this study it was still unclear whether noticeable amounts of pollutants reach the Saale (UBA, 2003). Apart from the industrial park at Leuna, other chemical plants are situated between Leuna and Halle, e.g. the Buna Works.

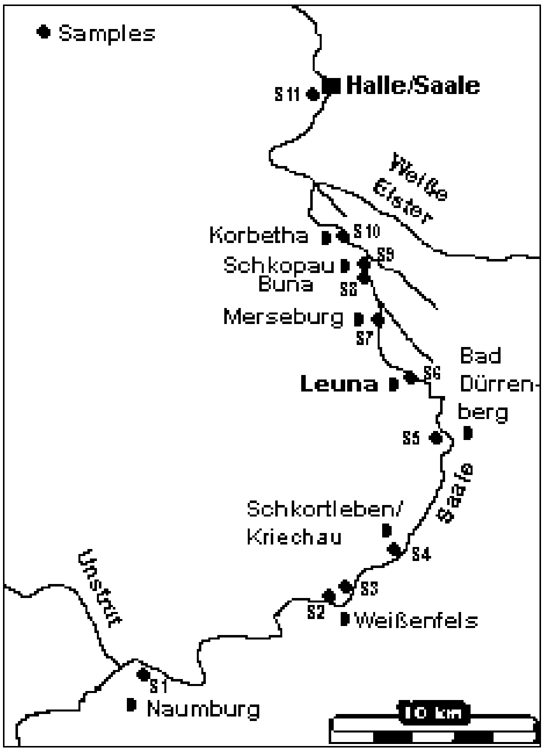

Figure 5-2: Location of sample collection from the river Saale from 11/18/02-11/19/02.

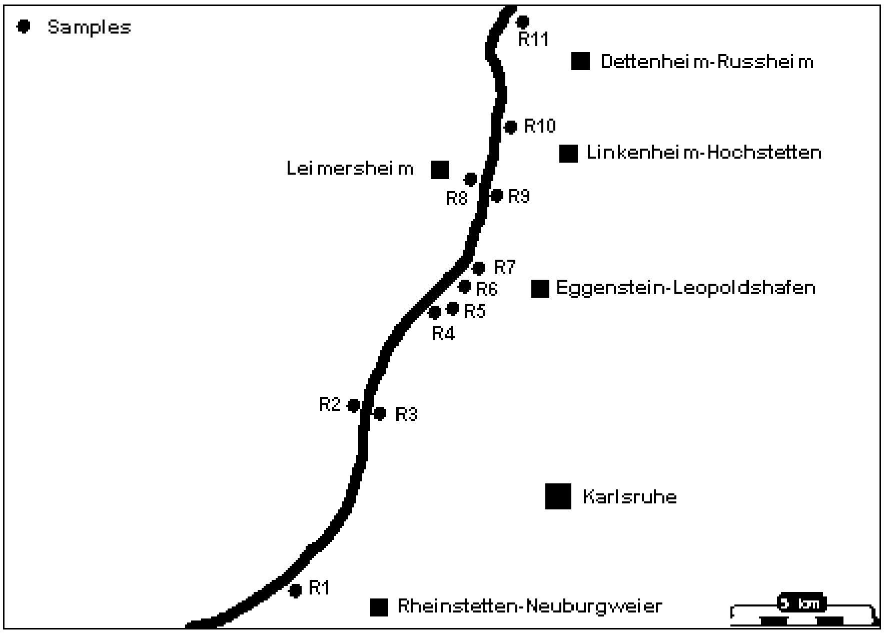

Figure 5-3: Location of sample collection from the river Rhine on 08/16/02.

In a previous study, spot sampling at the river Rhine was performed from 11/06/00-11/07/00 between Schaffhausen (Switzerland) and Wesel. Between Schaffhausen and Karlsruhe the

MTBE concentrations were low, except in one sample showing approximately 200 ng/L. Downstream from Karlsruhe, the maximum concentration of 383 ng/L was measured (Achten *et al.*, 2002a). This might be due to a refinery and the largest fuel tank farm in Germany at Karlsruhe. The wastewater of the refinery is discharged through a treatment plant into the Rhine (MIRO, 2003). In the present study, a more detailed sampling on 08/16/02 at the river Rhine consisted of samples taken between Neuburgweier (R1) and Russheim (R11) on a distance of about 30 km including the area around the refinery and the associated oil harbor (Figure 5-3). Approximately 150,000 t MTBE per year are produced in this refinery (Pahlke *et al.*, 2000). Due to another harbor and former oil industry with contaminated sites at the left bank of the river Rhine, two samples from the left bank were also collected (R2, R8).

5.3.2. Sampling and Analysis

River water grab samples were taken at a depth of about 30 cm below the surface of the water. The samples were stored in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. They were stored and transported at 4°C and analyzed within three weeks. During sampling and transport of water samples field blanks were always present and analyzed parallel to the samples. The analysis was performed by a combination of headspace-solid phase microextraction (HS-SPME) and gas chromatography/mass spectrometry (GC/MS). Mass chromatography of m/z 73 (MTBE) and m/z 76 (internal standard d_3MTBE) was used for quantitation. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. The detection limit was 10 ng/L with a relative standard deviation of 11%. Laboratory blanks were measured regularly. A detailed description of the analytical method is published elsewhere (Achten *et al.*, 2001b), with the exception of the used J&W Scientific DB-624 column (60 m x 0,32 mm) with a film thickness of 1.8 µm. The samples were checked additionally for benzene and toluene with the same method and a detection limit of 100 ng/L.

5.4. Results

5.4.1. Lippe/Wesel-Datteln-Canal

In 9 samples collected from the Lippe the median MTBE concentration was 274 ng/L, whereas the median concentration in 9 samples from the Wesel/Datteln-Canal was 133 ng/L. Along the course of the river Lippe the MTBE concentration decreased from Datteln/Ahsen (L1) to Haltern

(L2) from 274 ng/L to 87 ng/L. At Marl (L3) the concentration reached a value of 369 ng/L and decreased again to 131 ng/L between Marl and Hünxe (L3-L8) (Figure 5-4).

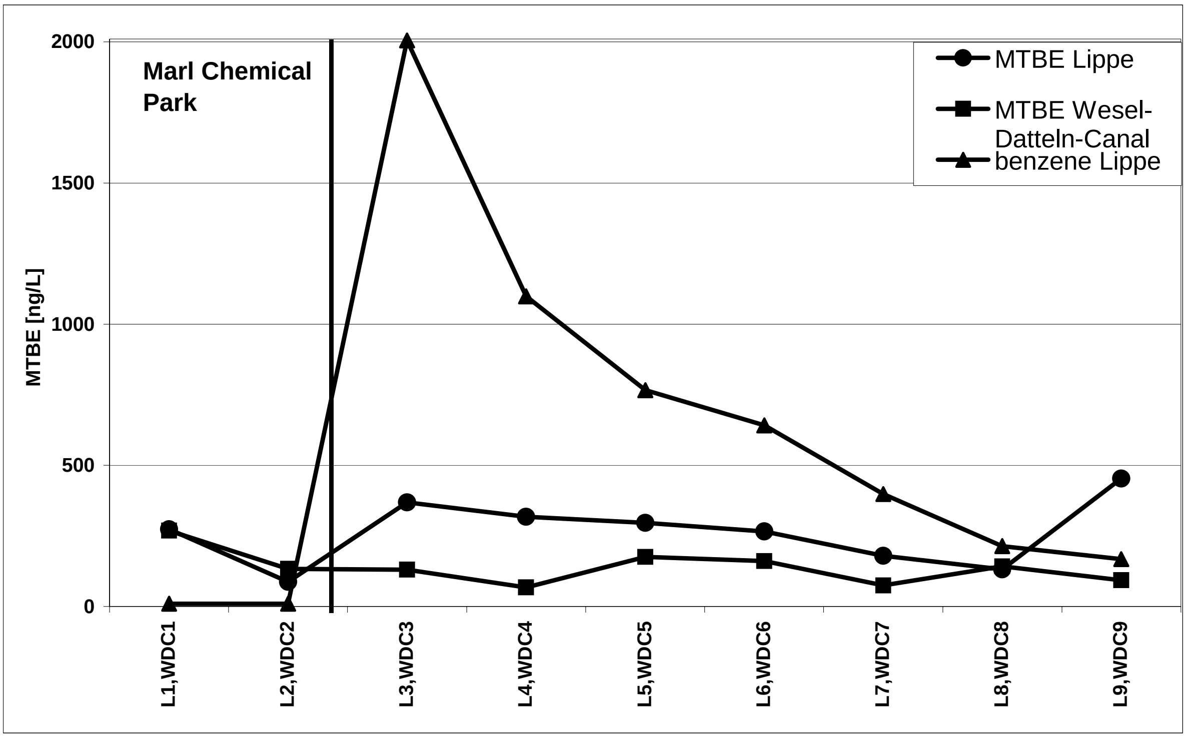

Figure 5-4: MTBE concentrations in Lippe and Wesel-Datteln-Canal water from 05/07/03-05/08/03. Circles and squares indicate MTBE in the Lippe and the Wesel-Datteln-Canal, respectively. Triangles indicate benzene in the Lippe. Method detection limit was 10 ng/L with a relative standard deviation of 11%. The sampling locations are shown in Figure 1. For single results see Appendix Table A2.

The maximum concentration (453 ng/L) was observed near the mouth at Wesel (L9). Only in the river Lippe benzene could be found in detectable amounts and similar to MTBE, the benzene concentrations also increased from <100 ng/L at Haltern (L2) to 2005 ng/L at Marl (L3), but the following decrease to 168 ng/L included the sampling site at Wesel (L9). At the Wesel-Datteln-Canal (Figure 5-4) the sampling campaign revealed a maximum concentration of 269 ng/L at Datteln/Ahsen (WDC1). In the further course of the canal, the concentrations fluctuated in a range of 68 ng/L to 176 ng/l (WDC2-WDC9). The samples taken at the river Rhine (Table A4 in the Appendix) showed a maximum concentration of 497 ng/L at Mehrum/Voerde (R12) and the concentrations decreased to 272 ng/L and 292 ng/L after the mouths of the canal (R13) and the Lippe (R14), respectively. The samples taken at the lower Rhine between Düsseldorf and

Emmerich including R12-R14 had a median concentration of 251 ng/L, which is in accordance to former investigations.

5.4.2. Saale

MTBE was detectable in all but one sample (S2) taken at the river Saale in a range of 13-387 ng/L. Between Naumburg (S1) and Bad Dürrenberg (S5) the median MTBE concentration was 24 ng/L and increased to 379 ng/L between Leuna (S6) and Halle (S11).

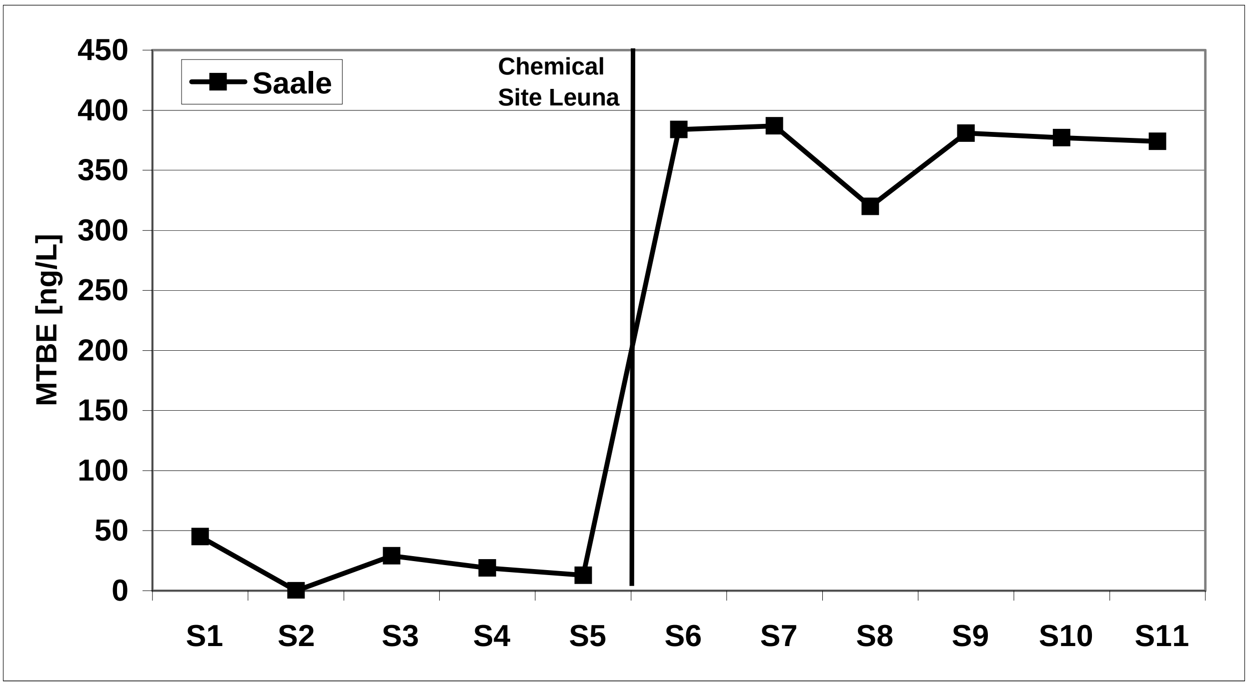

Figure 5-5: MTBE concentrations in Saale water from 11/18/02-11/19/02. Method detection limit was 10 ng/L with a relative standard deviation of 11%. For single results see Appendix Table A3.

Concentration ranges within the two parts were small, <10 ng/L to 45 ng/L (S1-S5) and 320 ng/L to 387 ng/L (S6-S11) (Figure 5- 5). In the Weisse Elster, an affluent of the Saale river, MTBE also was detectable at a concentration of 45 ng/L.

5.4.3. Rhine

The sampling at the river Rhine in the region of Karlsruhe on 08/16/02 revealed a median MTBE concentration of 368 ng/L. The two samples taken at the left bank (R2, R8) contained MTBE at concentrations lower than 100 ng/L.

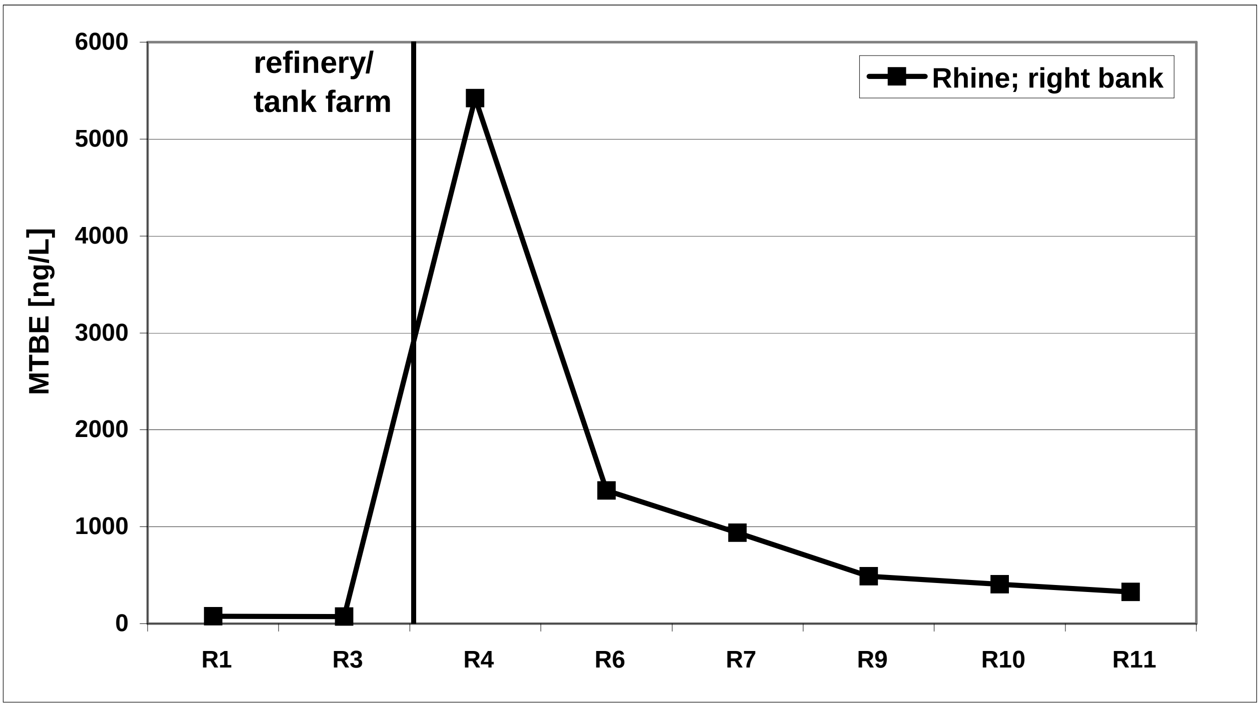

Figure 5-6: MTBE concentrations in Rhine water (right bank) on 08/16/02. Method detection limit was 10 ng/L with a relative standard deviation of 11%. For single results see Appendix Table A4.

The samples originating from the right bank (Figure 5- 6) between R1 and R3 also were below 100 ng/L, but at R4 the concentration increased to 5421 ng/L. Between R4 and R11 the concentration decreased to 328 ng/L. The sample taken in the oil harbor showed a concentration of 991 ng/L.

5.5. Discussion

5.5.1. Lippe/Wesel-Datteln-Canal

By summarizing all samples from the Lippe and the Wesel-Datteln-Canal, the median concentrations of 274 ng/L (Lippe) and 133 ng/L (Wesel-Datteln-Canal) are comparable to other German rivers and tributaries of the Rhine (Brauch *et al.*, 2000; Achten *et al.*, 2002a,). However, the occurrence of MTBE in the two streams most probably had different sources, if the direct input via precipitation is omitted.

A slightly increased concentration in the samples near to the mouth at Wesel occurred during the sampling at the river Lippe. This might be due to the influence of the river Rhine and/or a marina located nearby, at the right bank of the Rhine at Wesel. Concentrations higher than 100 ng/L were measured in all but one sample, probably because of inputs via sewage plant effluents. The Lippe and its affluents are used for sewage disposal: In the year 2000, 104 community sewage plants used the river as receiving stream, 42 of them treated waste water from more than 10,000 residents in each case (NRW, 2000). Sewage plant effluents containing domestic wastewater and urban runoff have been shown to be a source for MTBE in surface water. The concentrations in the effluents vary significantly and were shown to range between 13-3162 ng/L (Kolb *et al.*, 2003). These fluctuating discharges may explain the median MTBE concentration of 274 ng/L measured in the Lippe. Industrial effluents have also been shown to be important sources of MTBE that is diluted in the river water system. In the year 2000, the Lippe received about 23.58 Mio m^3 of industrial wastewater (NRW, 2000). The two water treatment plants of the chemical park in Marl use the Lippe as the receiving stream. 15,9 Mio m^3 of process wastewater were treated and discharged into the Lippe in the year 2002 (Chemiepark Marl, 2003). The proportion of wastewater originating from the MTBE producing plant was not available. Concentrations in wastewaters of a MTBE plant reported by the corresponding company were below 1000 ng/L (MEF, 2001). The increase of MTBE and benzene concentrations between Haltern (L2) and Marl (L3) might weakly reflect the influence of discharged water by the chemical park. Community sewage plants as possible MTBE sources are not present at the Wesel-Datteln-Canal (NRW, 2001). The occurrence of MTBE with a median concentration of 133 ng/L therefore might be due to shipping traffic. As part of the Western German Canals and the Federal Waterway of Germany, the canal is important for transit traffic (ELWIS, 2002). However, more important than freight traffic, recreational boating has been reported in several studies to be related to the occurrence of MTBE (Reuter *et al.*, 1998; Dale *et al.*, 2000; Brown *et al.*, 2001; An *et al.*, 2002; Zuccarello *et al.*, 2003). These studies mainly focused on lakes, marinas or reservoirs, and seasonal trends could be demonstrated. Recreational boating on the canal has increased: As part of the opening up of the Ruhr Basin region for sport boating, four new landing stages for boat tourists have been established at the canal since 1999 (NRW, 2003). Varying MTBE concentrations in the canal probably were the result of diffusive and intermittent MTBE input caused by recreational boating activities. Dilution and mixing is more effective in flowing water than in stratified water bodies. This and the fact that the present samples were taken at sites remote from any marinas as well as lower MTBE concentrations in German gasoline may explain the lower overall median concentration in the canal of 0.133 μg/L compared to concentrations ranging from <0.1 to 29 μg/L found in lakes of the U.S. (Reuter *et al.*, 1998; Dale *et al.*, 2000; An *et al.*, 2002;) or in a recreational harbor (Zuccarello *et al.*, 2003). Beside shipping and boating traffic, MTBE occurrence in the canal might be due at least partly to water taken from the Lippe to feed the canal system. Studies conducted at the Lippe and the Western German Canals which investigated the occurrence of pesticides have shown that the pesticide load of the Lippe corresponds to the pesticide load in the adjacent canals (NRW, 1997). However, the concentrations of the pollutants in the canals were mostly lower. Investigations in the year 1994 revealed lower pesticide contents in the Wesel-Datteln-Canal than in the Dortmund-Ems-Canal and the Datteln-Hamm-Canal, where the feed-in is located.

5.5.2. Saale

The MTBE concentrations in samples from the river Saale measured during this study can be divided into two parts. The first part, represented by samples collected between Naumburg (S1) and Bad Dürrenberg (S5) with concentrations between <10 ng/L and 45 ng/L, reflects the situation typical for smaller rivers with very restricted shipping traffic (Land Sachsen-Anhalt, 2001). Nevertheless, the Saale and its affluents are also used for community wastewater disposal and were already studied for model calculations (Schröder and Matthies, 2002). This influence was not visible in this part of the river during the sampling campaign. The part further downstream of the river, between Leuna (S6) and Halle (S11), revealed MTBE concentrations with a median value of 379 ng/L, 16 times the median value in the first part, and a small range of only 320-387 ng/L. This significant increase after Bad Dürrenberg (S5) can be related to the MTBE contaminated site at Leuna. Despite the protective measures that were already initiated (UBA, 2003) at the affected site, some MTBE still reaches the Saale as the receiving stream. However, it should not be neglected that the wastewater disposal facilities of the chemical site Leuna are also discharging wastewater into the Saale. Apparently, MTBE may reach the Saale river despite the presence of a prevention system installed for the protection of the Saale (Infra Leuna, 2003). Additionally, the zone of restricted shipping traffic ends at Kreypau between Bad Dürrenberg (S5) and Leuna (S6), and from this point the Saale is part of the Federal Waterway of Germany (Land Sachsen-Anhalt, 2001). Shipping and boating activities also might be a possible MTBE source in the second part of the river. However, during the sampling campaign shipping activities on the river were rare. The small range of MTBE concentrations between Leuna (S6) and Halle (S11) clearly indicates a MTBE source between S5 and S6 that is discharged into the river. A significant downstream dilution of MTBE between Leuna (S6) and Halle (S11) is not detectable. Even downstream from the affluent Weisse Elster, where only 45 ng/L MTBE could be measured, the concentration remained at a constantly high level. MTBE contaminations in flowing water originating from boating activity should be more fluctuating, like at the Wesel-Datteln-Canal.

5.5.3. Rhine

At the river Rhine, all possible sources for MTBE in river water are present. Further to the direct input via precipitation, MTBE in the Rhine may originate from sewage plants, shipping traffic or industrial input. The sampling at the Rhine on the 11/06/00-11/07/00 revealed higher concentrations of MTBE near urban agglomerations and an increasing concentration between the sample locations before (Rastatt, 138 ng/L) and after Karlsruhe (Leopoldshafen, 383 ng/L) (Achten *et al.*, 2002a). Increasing concentrations between two corresponding sampling sites from 76 ng/L at Rheinstetten/Neuburgweier (R1) to 488 ng/L at Leopoldshafen (R9) were also found in the present study. The significant increase of the MTBE concentrations between R1 and R11 indicates the presence of a point source infiltrating MTBE into the river. Between R3 and R4 the MTBE contents increased from a background concentration of 73 ng/L to 5421 ng/L at the area of the refinery/tank farm (R4). The release of MTBE into the Rhine between R3 and R4 might occur either through contaminated groundwater or through tank bottom water released from the tank farm, despite large precautions at the facility (MIRO, 2003). After the refinery area and the oil harbor, between R6 and R11, the MTBE content constantly decreased to reach 328 ng/L at R11. Compared to the Saale, the high water flow and strong vorticity in the river Rhine supports the dilution of MTBE within a shorter distance: The average flow of the Rhine at the level Maxau from 1931-2001 was 1270 m^3/s, whereas the average flow of the Saale at the level Naumburg-Grochlitz from 1934-2000 was 67.8 m^3/s (Wiechmann, 2003). The sample taken at the oil harbor (R5) close to the refinery showed a concentration of 991 ng/L, probably due to releases from leaking loading/unloading facilities. Compared to the right bank of the Rhine at the studied site, the samples taken at the left bank were less affected by MTBE and only showed concentrations of 88 ng/L and 67 ng/L.

5.5.4. General Aspects

One aim of the present study was to investigate the influence of MTBE production/formulation/storage sites and/or related groundwater contaminations on the occurrence of MTBE in receiving streams. MTBE was found at detectable amounts in all but one sample during the present study and the median concentrations of 133-368 ng/L are comparable to results of other studies investigating MTBE in German and European surface waters (MEF, 2001, Püttmann *et al.*, 2002). Two samples had concentrations higher than 1 µg/L, and in only one of them MTBE was detected at a concentration of about 5 µg/L.

The different concentration profiles that were found at the three different study sites clearly indicate an MTBE input through the possible sources at the river Saale, the river Rhine, but not at the river Lippe. At the Leuna site, the Saale is the receiving stream for the upper aquifer of a MTBE contaminated site (UBA, 2003) and it seems likely that the increasing MTBE concentrations are due to this groundwater input. The high MTBE concentrations in the Rhine at Karlsruhe most probably originate from the refinery/tank farm, but the pathway of infiltration into the river is still unclear.

The results of this study are important in relation to PECs from the EU risk assessment and the findings using the EQC model (MEF, 2001; Achten *et al.*, 2002c). Compared to default EUSES calculations of 10.3 mg/L and 0.442 mg/L as PECs in surface water at production and formulation sites, respectively (MEF, 2001), the concentrations found within this study were one or two orders of magnitude lower. If site specific information was available for calculations within the risk assessment, the PECs ranged from <30 ng/L to <2.5 mg/L (MEF, 2001), depending on the MTBE concentration in the sewage treatment plant effluent of the production/formulation site and the dilution factor of the receiving stream. The lower part of this concentration range is more comparable to the findings of the present study. The calculations using the EQC model revealed a lower average MTBE concentration in German surface water of 19 ng/L compared to the measured average concentration in the years 1999/2000 of 50 ng/L (Achten *et al.*, 2002c). The findings of the present study indicate that different additional source emissions that have yet not been taken into consideration or have been underestimated, could at least in part explain this difference. At the river Rhine and the river Saale, examples of MTBE releases from point sources have been localized and were shown to increase MTBE concentrations significantly in the receiving water. However, estimations about annual emissions into water could not be made, since the investigation of the spatial distribution at the investigated streams are only snap-shots. Monitoring data from year-round sampling at such sites would be useful for further modelling. Especially the release of tank bottom waters at terminal sites may only cause intermittent discharges. They are seen as the most pronounced source of MTBE to surface water from these sites, leading to high peak concentrations and large emitted volumes with concentrations up to 4000 mg/L resulting in a local PEC of 60 mg/L (MEF, 2001). Although there is a lack of year-round sampling at the sites investigated in the present study, it can be concluded that the assumption of an aqueous MTBE emission rate of 50 t/a in Germany when using the EQC model (Achten *et al.*, 2002c) is most probably too low, since further MTBE production sites in Germany are located in places where similar interrelated conditions may exist. Other sources than contaminated groundwater or production/formulation/storage sites are losses from gasoline distribution and gasoline-fueled watercraft. These sources might have also been underestimated in the EQC calculation. The sample taken at the oil harbor at the Karlsruhe site and the MTBE occurrence in the Wesel-Datteln-Canal may be references to these sources. The local PEC at sites with surface water boarding was assumed to be 12 µg/L, whereas the emissions to surface water during transportation and at loading/unloading harbor facilities were considered to be out of the scope of the risk assessment (MEF, 2001). The importance of recreational boating was shown in a study regarding inputs and coastal receiving waters in Southern California (Brown *et al.*, 2001). Refineries and public-owned treatment works (POTWs) were shown to contribute the highest mass emissions from various inputs (POTW, refinery, dry weather stream, stormwater) to the marine environment and mean concentrations of up to 1878 µg/L were measured in discharges of a petroleum refinery. Nevertheless, the highest concentrations in receiving waters were found in marinas. Similar to the detected point sources at the Rhine and the Saale, the possible releases from processing sites, where MTBE is used as solvent or reagent, community sewage plants, urban runoff and direct input from the atmosphere via precipitation have been investigated to date only partially (Kolb *et al.*, 2003), and should be investigated in future studies.

6. MTBE IN SNOW SAMPLES IN GERMANY

6.1. Abstract

In the present study, 43 snow samples from 13 different locations from Germany and Switzerland (2 locations) were taken and analysed for their MTBE content at a detection limit of 10 ng/L. MTBE could be detected in 65% of the snow samples at concentrations ranging from 11 ng/L to the maximum concentration of 631 ng/L at the monitoring station Schmücke. The MTBE amounts that were found in the collected snow samples were often higher (>100 ng/L) than formerly analysed rainwater samples. This confirms previous observations of other contaminants showing that snow is a more effective scavenger for organic contaminants than rain. Similar MTBE contents of 108-127 ng/L were measured in three concurrent snowpack samples taken at different locations within the city of Frankfurt/Main. The samples collected at rural and urban locations did not show significant differences in mean MTBE concentrations. The MTBE amounts that could be found even in the snow samples from rural and remote areas may be explained by moving air masses, the lower photochemical degradation of MTBE in wintertime and the ability of snow to significantly scavenge gas phase impurities from the atmosphere. A temperature dependency of the MTBE snow concentrations and a wash-out effect could be observed in samples from the monitoring stations Schauinsland and Taunus-Observatorium (Kleiner Feldberg).

6.2. Introduction

Snow and ice are important for the troposphere and the ecosystem because of the influence on energy balances and hydrological fluxes. Additionally, snow contributes as an effective scavenger to the removal of pollutants from the atmosphere in temperate and polar regions. The uptake of solid, liquid and gas phase impurities by snow and ice includes inorganic and organic compounds (Hoff *et al.*, 1995; Schwikowski *et al.*, 1998; Baker, 1999). The snow scavenging of hydrophobic organic chemicals was reviewed by Wania *et al.* (1998). Once the snow is on the ground, some pollutants may affect the quality of natural waters and may furthermore be found in drinking water sources (Czuczwa *et al.*, 1988). This transfer pathway has to be considered particularly for compounds like methyl *tert*-butyl ether (MTBE), characterised by relative high water solubility, slow photochemical degradation near metropolitan areas and a low biodegradation rate in water (Squillace *et al.*, 1996).

The oxygenate MTBE is added to gasoline in order to increase its octane level and to reduce the emission of carbon monoxide and hydrocarbons from vehicles resulting in a lowering of the ozone levels in the air. 98.5% of the MTBE produced in the EU is used for gasoline blending (MEF, 2001). The annual demand of MTBE in Europe today is about 3 million tons, approximately equal to the production capacity (EFOA, 2003). In Germany, about 683,900 tons were added to gasoline in 2001 (Sur *et al.*, 2003). The MTBE concentration in Eurosuper, the most commonly used gasoline in Germany in 2001, is about 3% (w/w). The amounts in regular and super premium gasoline are 0.43% (w/w) and 10.2% (w/w), respectively (Sur *et al.*, 2003). The release and distribution of MTBE in the aquatic environment has led to concern about the occurrence of MTBE in drinking water (Clawges *et al.*, 2001). Further to the potential toxicological effects on human health, MTBE concentrations as low as 2-2.5 micrograms per liter (μg/L) may lead to objectionable taste and odour detections by sensitive subjects (Borden *et al.*, 2002).

MTBE can be emitted into groundwater and surface water through a variety of sources, including point source releases from leaking underground storage tanks (Johnson *et al.*, 2000) and direct emission of MTBE contaminated water at industrial sites where MTBE is produced or used as solvent (Kolb *et al.*, 2003). In groundwater, a value of 1-5 μg/L may be suitable to distinguish between point sources and diffusive sources (Schmidt *et al.*, 2003). Community sewage plant effluents and urban runoff are more diffusive sources (Achten *et al.*, 2001c; Achten *et al.*, 2002a). The urban atmosphere as possible diffusive source of MTBE was first investigated by Pankow *et al.* (1997). Evaporative and exhaust emissions to air from the use of gasoline have been proposed to be the main source of MTBE to the environment (MEF, 2001). MTBE air emissions in Germany of 2285 t in the year 1999 were estimated (Pahlke *et al.*, 2000). Monitoring of ambient MTBE air concentrations at service stations in Finland revealed mean concentrations of 4.1-14.1 $\mu g/m^3$ and 247-1,347 $\mu g/m^3$ at sampling points in the vicinity of service stations and in the centre of the pump island, respectively (Vainiotalo *et al.*, 1998). The deposition of MTBE from the atmosphere by precipitation was investigated in several studies revealing MTBE concentrations in precipitation in Germany (Achten *et al.*, 2001c) and stormwater in the U.S. (Squillace *et al.*, 1996; Borden *et al.*, 2002) of <10-85 ng/L and <50-13,470 ng/L, respectively. Regarding the U.S. data, it should be considered that MTBE in stormwater in the U.S. could be associated with urban land surfaces (Lopes and Bender, 1998), that the average percent of impervious surface possibly correlates with MTBE concentrations (Lopes and Bender, 1998) and that higher MTBE concentrations could be associated with runoff from gas stations (Borden *et al.*, 2002). Nevertheless, urban air is potentially an important source of MTBE in urban waters because the detection frequencies in stormwater in the U.S. were seasonally dependent (Lopes and Bender, 1998). The data on MTBE in precipitation in Germany also showed a seasonal trend, since MTBE was only detectable in wintertime at temperatures lower than about 10-15°C (Achten *et al.*, 2001c). In contrast to the stormwater data obtained in the U.S., this trend might be more related to ambient meteorological conditions because the MTBE concentrations in German gasoline are nearly constant all year round.

In the summer, when enhanced photochemical activity occurs, more MTBE will be attacked by hydroxyl radicals and will be degraded to *tert*-butyl formate (TBF). The atmospheric half-life times in summer and winter are approximately 3 and 6 days respectively (Wallington *et al.*, 1988; Squillace *et al.*, 1996; Achten *et al.*, 2002c). The longer half-life time and moving air masses therefore may contribute to positive MTBE detections even in rural precipitation during wintertime. This could be observed in a previous investigation of 7 snow samples collected at rural sites in Germany (Achten *et al.*, 2001c). The objective of the present study was to investigate a larger amount of snow samples from all over Germany with respect to their MTBE content. The sampling included urban sites like Frankfurt/Main (Frankfurt/M) as well as rural sites or remote monitoring stations. The data were compared to available meteorological data in order to investigate possible patterns when MTBE was detectable.

6.3. Experimental

Spot sampling of fresh snow was performed from 2001-2003 at one urban (Frankfurt/M) and 12 rural locations at altitudes from 113 m up to 3450 m. 12 samples were collected at the monitoring stations Schmücke, Brotjacklriegel, Schauinsland and Zugspitze by the Umweltbundesamt (UBA). 9 samples from the Taunus-Observatorium (Kleiner Feldberg) were taken by the Institut für Meteorologie und Geophysik of the University Frankfurt/M. Snow samples in Frankfurt/M-City were collected through a wet-only rainwater collector on top of a building. The remaining samples were taken in glass jars placed on the ground during the snow events. The samples taken at different locations of Frankfurt/M on 02/09/02, as well as the samples taken at Dammbach, Sourbrodt (Belgium), Kandel, Kleine Scheidegg (Switzerland) and Jungfraujoch (Switzerland) were collected directly from snow layers far away from any road traffic by sweeping the fresh snow from the underlying snowpack. The meteorological data were provided by the UBA, Deutscher Wetterdienst (DWD), Hessisches Landesamt für Umwelt und Geologie (HLUG) and Institut für Meteorologie und Geophysik of the University Frankfurt/M. After thawing, the samples were stored in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. All samples were stored and transported at 4°C and analysed within three weeks. During sampling and transport always field blanks were present and analysed parallel to the samples. The analysis was performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS). Due to the origin of the samples, high levels of monoaromatic compounds (benzene, toluene and xylenes) could not be observed, which means that there was no limitation for the use of SPME as analytical method (Black and Fine, 2001). Mass chromatography of m/z 73 (MTBE) and m/z 76 (internal standard d_3MTBE) was used for quantitation. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. The detection limit was 10 ng/L with a relative standard deviation of 11%. Laboratory blanks were regularly measured. A detailed description of the analytical method is published elsewhere (Achten *et al.*, 2001b), except that a J&W Scientific DB-624 column (60 m x 0,32 mm) with a film thickness of 1.8 µm was used as chromatographic column.

6.4. Results and Discussion

The measured MTBE concentrations and available meteorological conditions during the sampling events are given in Table 6-1. MTBE was detected in 28 of 43 samples (65%). The concentrations varied from non-detectable to 631 ng/L. 17 samples had concentrations higher than 100 ng/L. The former study conducted by Achten *et al.* (2001c) revealed MTBE concentrations below 100 ng/L in both rain water samples and 7 snow samples taken at comparable locations. This difference in the observed concentration range comparing both studies can be explained by the fact that in the present study only snow samples and no rain samples were analyzed. The overall higher MTBE concentrations in snow might be due to the fact that snow has the potential to accumulate airborne contaminants by washing out the aerosol and by sorbing volatile contaminants on its particles as it provides a greater surface area compared to rain droplets (Viskari *et al.*, 1997; Wania *et al.*, 1998; Franz and Eisenreich, 1998). Organic pollutants like alkyl benzenes were also observed to be more abundant in snow samples than in rainwater samples (Czuczwa *et al.*, 1988) and higher snow scavenging ratios than rain scavenging ratios for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined (Wania *et al.*, 1998).

In the present study, maximum concentrations of 438 ng/L and 631 ng/L MTBE were measured in samples that were collected at the monitoring station Schmücke. The reason for these high concentrations is not yet clear but might be due to particular meteorological conditions at this site. These conditions imply a significant transfer of air masses, that possibly contain pollutants, from the valley area into clouds at the Schmücke mountain, where the monitoring station is located (Jaeschke *et al.*, 2004). The three sampling locations in Frankfurt/M (F-Schwanheim, F-Sossenheim, F-Lohrberg) are in a range of 4-8 km away from Frankfurt/M-City. Snowpack samples were collected at these locations on 02/09/02. The results from the analyses of these samples revealed similar MTBE contents of 108 ng/L – 127 ng/L. The air concentrations of MTBE at the three different sites within Frankfurt/M were similar assuming that local car exhaust is the major source of MTBE in these samples and assuming there is an equilibrium of MTBE between the fallen snow and the ambient air within a fall distance of 10 m (Borden *et al.*, 2002). Annual mean urban air concentrations of MTBE measured in Helsinki (Finland) were in reasonably good agreement at four different sites within the city. The annual cycles of MTBE were shown to be very similar and maximum concentrations were at least in part due to low wind speeds (Hellen *et al.*, 2002). The wind speeds in the area of Frankfurt/M during all sampling days were moderate breeze (data not shown). Therefore, the fact that the remaining Frankfurt/M samples with concentrations below 100 ng/L were taken on top of a building 15 m above the ground, may have played an important role in terms of lower MTBE concentrations measured. Additionally, these samples were collected by a rainwater collector in contrast to the snowpack samples from 02/09/02, where the higher concentrations may indicate a contribution of directly sorbed pollutants (Wania *et al.*, 1998). The median concentration of MTBE in the seven snow samples from Frankfurt/M of 54 ng/L is comparable to the median concentration of 47 ng/L in six snow samples collected throughout the Denver metropolitan area in the U.S. (Bruce and McMahon, 1996). Compared to Frankfurt/M, the remaining samples originated from remote monitoring stations or rural areas defined by population densities below 386 people per km^2 (Moran *et al.*, 1999).

Sampling Location	Altitude [m]	Sampling Date	Temperature [°C]	Precipitation [mm]	MTBE [ng L^{-1}]
Frankfurt/M-City	113	01/19-20/02	4,0	7,2	30
Frankfurt/M-Schwanheim*	113	02/09/02	9,8	10,5	113
Frankfurt/M-Sossenheim*	113	02/09/02	9,8	10,5	108
Frankfurt/M-Lohrberg*	113	02/09/02	9,8	10,5	127
Frankfurt/M-City	113	02/22/02	1,9	6,4	42
Frankfurt/M-City	113	03/14/02	4,8	4,9	54
Frankfurt/M-City	113	01/13/03	-3,0	1,2	16
Endingen	187	12/23/01	-3,5	1,4	43
Endingen	187	12/19-20/01	0,05	0,6	174
Homberg/O	282	11/23/01	n.a.	n.a.	47
Homberg/O	282	11/23/01	n.a.	n.a.	<10
Dammbach*	524	02/09/02	10	9,8	120
Sourbrodt/Hohes Venn (B)*	557	02/09/02	n.a.	n.a.	75
Kleiner Feldberg/Ts	825	12/19/01	-2,5	4,2	78
Kleiner Feldberg/Ts	825	02/09/02	4,0	13,5	111
Kleiner Feldberg/Ts	825	02/18-19/02	-2	8	247
Kleiner Feldberg/Ts	825	02/20-21/02	-2,3	6,2	<10
Kleiner Feldberg/Ts	825	01/06-07/03	-9,3	0,65	155
Kleiner Feldberg/Ts	825	01/30-31/03	-7,5	3	61
Kleiner Feldberg/Ts	825	02/03-04/03	-3,8	4,5	37
Kleiner Feldberg/Ts	825	02/04-05/03	-5,0	4,5	11
Kleiner Feldberg/Ts	825	02/05-06/03	-5,5	2,55	33
Schmücke	937	12/16-17/02	-1,3	3,3	438
Schmücke	937	01/13-14/03	-4,5	6,7	631
Brotjacklriegel	1016	12/16-17/02	-0,3	3,2	126
Brotjacklriegel	1016	12/31/02-01/01/03	-0,7	2,0	<10
Brotjacklriegel	1016	01/14-15/03	-1,8	0,3	<10
Brotjacklriegel	1016	01/31/03-02/01/03	-7,7	0,1	<10
Kandel *	1142	01/03/02	n.a.	n.a.	21
Schauinsland	1205	01/06/03	-8,6	0,4000	91
Schauinsland	1205	01/13/03	-4,5	5,3000	42
Schauinsland	1205	01/16/03	-2,0	1,4000	17
Schauinsland	1205	01/19/03	1,0	11,3000	<10
Kandel*	1241	01/03/02	n.a.	n.a.	222
Kl. Scheidegg (CH)*	2061	04/05/02	n.a.	n.a.	<10
Kl. Scheidegg (CH)*	2061	04/05/02	n.a.	n.a.	<10
Zugspitze	2650	04/22/03	-5,8	6,6000	<10
Zugspitze	2650	04/22/03	-5,8	6,6000	<10
Jungfraujoch (CH)*	3450	04/05/02	n.a.	n.a.	<10
Jungfraujoch (CH)*	3450	04/05/02	n.a.	n.a.	<10
Jungfraujoch (CH)*	3450	04/05/02	n.a.	n.a.	<10
Jungfraujoch-Sphinx (CH)*	3450	04/05/02	n.a.	n.a.	<10
Jungfraujoch (CH)*	3450	04/05/02	n.a.	n.a.	<10

*Table 6-1: Sample locations and measured MTBE concentrations in snow. When a sample was taken during two days, the ambient temperatures and amounts of precipitation are mean values; n.a. = not available. *snowpack samples.*

With exception of the locations Kleine Scheidegg (CH), Zugspitze and Jungfraujoch (CH), MTBE was detectable in snow samples from the rural locations, at least in one sample at concentrations similar to the urban samples (Figure 6-1). This is in contrast to MTBE air measurements and MTBE detections in rainwater. Urban air in Europe was shown to contain mean MTBE concentrations from 0.9 µg/m^3 – 2.8 µg/m^3, whereas at rural locations MTBE air concentrations ranged from 0.146 µg/m^3 – 0.78 µg/m^3 in recent studies (Hellen *et al.*, 2002; BUWAL, 1999, UMEG, 2002). The investigation of precipitation sampled throughout Germany revealed similar patterns, since MTBE was more often detectable in urban (86%) than in rural (18%) samples (Achten *et al.*, 2001c).

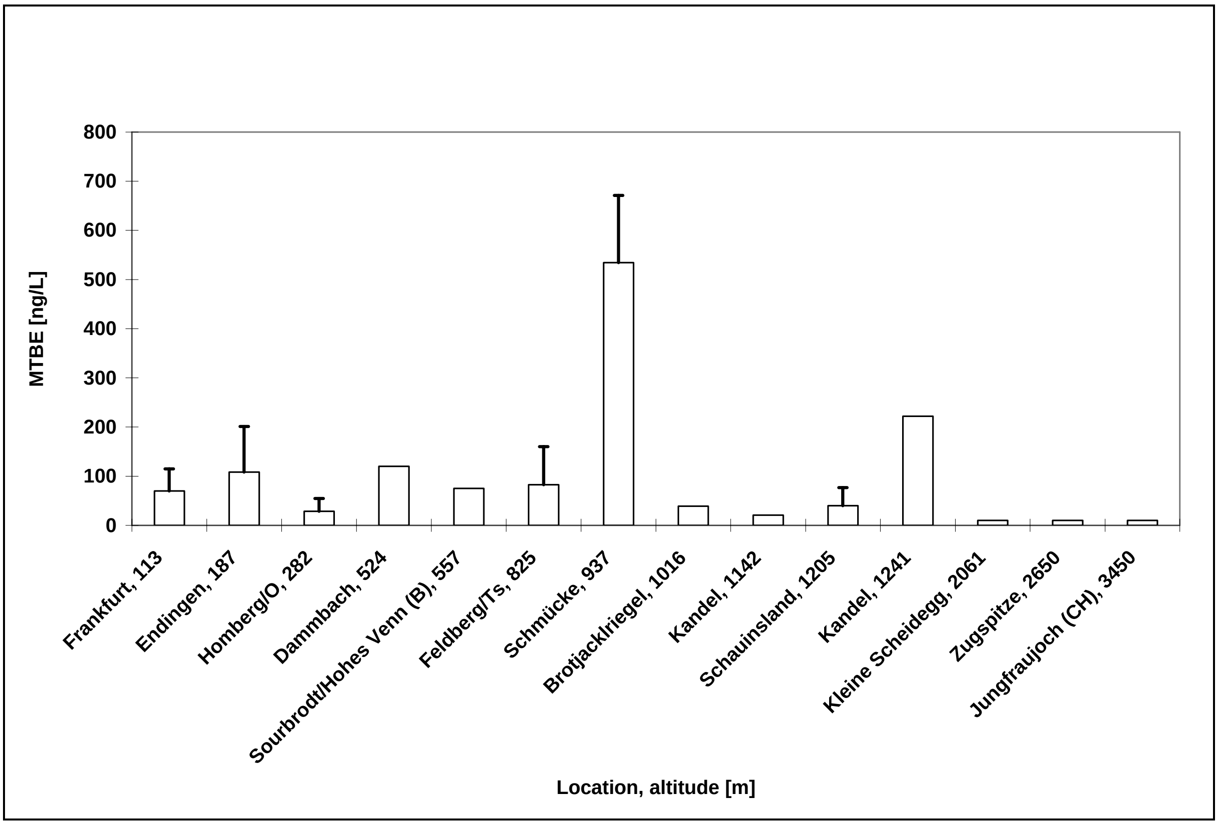

Figure 6-1: Mean MTBE concentrations and standard deviations in snow samples from different sampling locations. Samples <10 ng/L were calculated as 10 ng/L. For single results see Appendix Table A5.

Organic contaminants in snow cannot be easily related to the environment in which the snow sample was collected (Baker, 1999), because of the long-range transport of pollutants in the atmosphere by moving air masses (Kawamura *et al.*, 1996) and less photochemical activity in winter. However, in addition to the moving air masses, the occurrence of MTBE in snow collected at rural sites with similar or higher concentrations compared to that in urban samples may be explained by the above mentioned potential of snow fall to collect airborne contaminants by washing out the aerosol and sorption of MTBE from vapor (Viskari *et al.*, 1997; Wania *et al.*, 1998). The later discussed temperature dependence of the Henry's law constant may also explain the MTBE findings in the rural samples.

An example for the time dependent variation of MTBE concentrations in snow can be seen by the comparison of samples collected in January 2003 at the monitoring station Schauinsland (Figure 6-2).

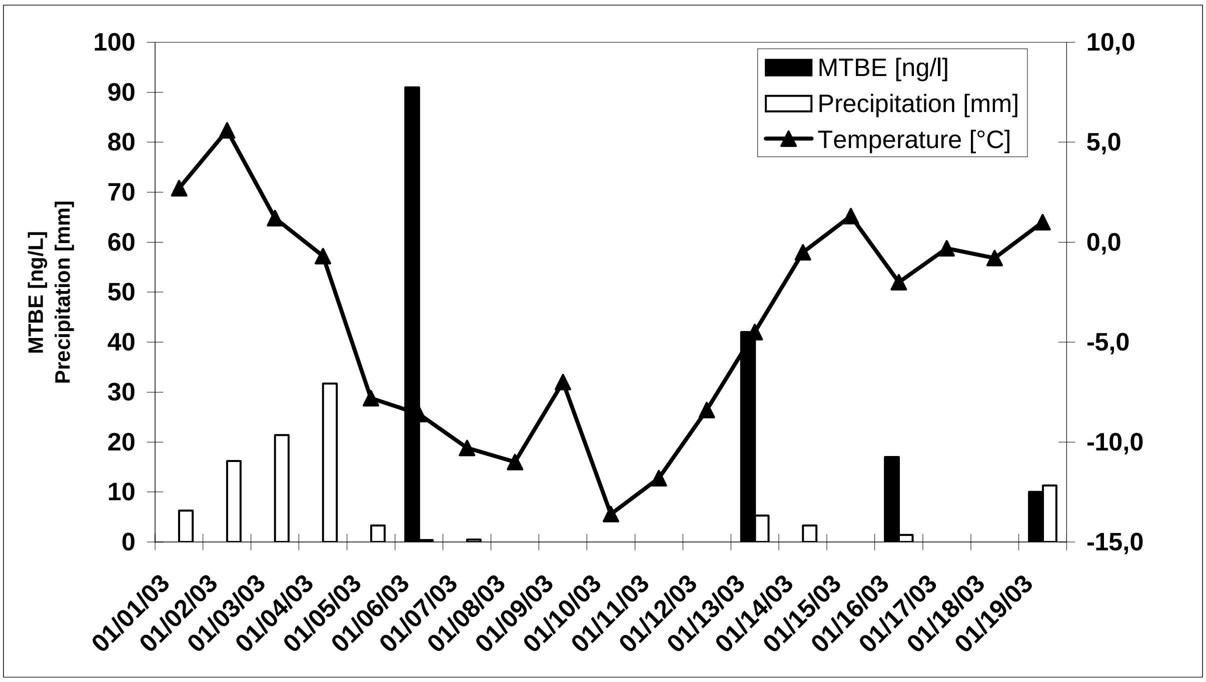

Figure 6-2: Measured MTBE concentrations in snow samples collected in January 2003 at the monitoring station Schauinsland versus ambient temperatures and amounts of precipitation. Samples <10 ng/L were calculated as 10 ng/L. For single results see Appendix Table A5.

The analysis of the first sample taken on 01/06/03 revealed an MTBE concentration of 91 ng/L, followed by decreasing concentrations of 42 ng/L, 17 ng/L and non-detectable MTBE amounts on 01/13/03, 01/16/03 and 01/19/03, respectively. The decreasing concentrations were accompanied by increasing ambient temperatures of -8.6°C on 01/06/03 and -4.5°C, -2°C and 1.0°C on 01/13/03, 01/16/03 and 01/19/03, respectively. This suggests a temperature dependence of the amounts of MTBE scavenged during the snow events. The snow samples were collected during single snow events. Between these snow events no heavy precipitation events occurred which allows to exclude the decrease of MTBE concentrations in the atmosphere by intermediate wash-out events. The wind direction during the days of sampling changed from NE at the beginning (01/06/03) to SW during the remaining sampling days. Thus, the influence of MTBE that originates from vehicle traffic sources on the air masses that reach the monitoring station Schauinsland could be expected to be higher during sampling from 01/13/03 to 01/19/03. This is not reflected by the analytical results which indicate that wind direction is not the most important factor for the MTBE concentration in precipitation (snow). Wind speeds on the days of sample collection ranged only between light air and gentle breeze. A major influence of wind speed on scavenging of MTBE cannot be derived from the data.

The data obtained from the samples collected at the monitoring station Schauinsland clearly show that increasing ambient temperatures correspond to the decreasing MTBE concentrations in the samples. Since the uptake mechanism of MTBE from the atmosphere by snow is still unclear, the Henry's Law constant (H) might be an appropriate parameter for a first approximation of the MTBE scavenging as a function of ambient temperatures. The occurrence of liquid phase chemistry (quasi liquid layer, QLL) on the surfaces of ice particles at temperatures down to -60°C has been described in laboratory studies and the liquid layer has been suggested to be stabilised by inorganic and organic solutes lowering the freezing point (Baker, 1999). The contribution of solution in the hypothetical QLL to the retention volume in inverse gas chromatography (IGC) experiments conducted with snow samples at –6.8°C was calculated up to 70%, dependent on the QLL thickness (0.1-50 nm) (Roth *et al.*, 2004). Although the QLL is not believed to behave as a bulk liquid (Domine and Thibert, 1996), the snow sorption coefficients of polar organic compounds are in the same range as extrapolated water surface coefficients of polar organic compounds (including MTBE with a quotient of 1.0) at -6.8°C (Roth *et al.*, 2004). On the basis of the hypothetical QLL, the variation of the Henry's law constant of MTBE at different temperatures may contribute to the understanding of the measurements at the monitoring station Schauinsland. Measured gas scavenging ratios and amounts of organic trace gases detected in cloud water are sometimes higher than those predicted from available H values. This difference may be explained by adsorption of the organic compounds on the droplet surface (Djikaev and Tabazadeh, 2003) or by missing H values determined at lower temperatures. Most Henry's law coefficients available in literature were determined at 20^{o}C or 25^{o}C. For many organic compounds H decreases by a factor of two for every decrease in temperature by 10°C (Ligocki *et al.*, 1985). This is also valid for MTBE, with a H value of $5.38*10^{-4}$ m^3 atm/mol at 20°C and a H value of $2.72*10^{-4}$ m^3 atm/mol at 10 ^{o}C (Fischer *et al.*, 2004). The water solubility of MTBE at 5°C is about twice the solubility at room temperature. MTBE behaves like a gaseous compound and therefore H can be calculated from water solubility and vapor pressure. The calculated H value of MTBE at 0°C is $1{,}29 \cdot 10^{-4}$ m^3 atm/mol (Fischer *et al.*, 2004), which is four times lower than the H value at 20°C. These properties of MTBE support the observed correlation between decreasing MTBE concentrations and increasing ambient temperatures in the Schauinsland samples and may also explain the MTBE findings in rural snow samples.

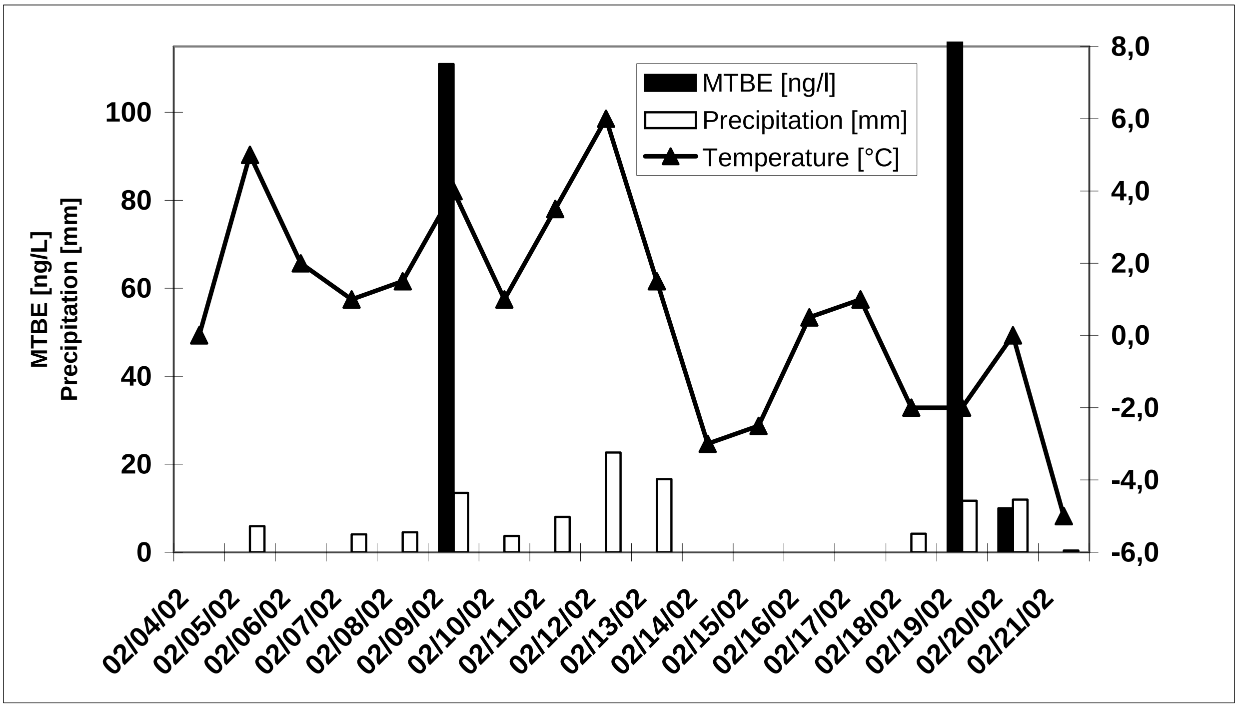

Figure 6-3: Measured MTBE concentrations in snow samples collected in February 2002 at the monitoring station Taunus-Observatorium (Kleiner Feldberg) versus ambient temperatures and amounts of precipitation. Note that the samples that are represented on 02/19/02 and 02/20/02 were taken from 02/18/02-02/19/02 and from 02/20/02-02/21/02, respectively. Samples <10 ng/L were calculated as 10 ng/L. For single results see Appendix Table A5.

Figure 6-3 shows the measured MTBE concentrations in snow samples taken in February 2002 at the monitoring station Taunus-Observatorium (Kleiner Feldberg). MTBE could be detected in a sample collected on 02/09/02 at a concentration of 111 ng/L. After a period with nearly no precipitation, snow sampling from 02/18/02 to 02/19/02 revealed an MTBE concentration of 247 ng/L, followed by non detectable MTBE amounts in the sample from 02/20/02 to 02/21/02. This decrease might be due to a wash-out effect as well as to the increase of the ambient temperature from -2°C on 02/19/02 to 0°C on 02/20/02. The subsequent temperature decrease to -5°C on 02/21/02 should not be taken into account, since the main part of the sample from 02/20/02 to

02/21/02 originated from 02/20/02, which can be seen by the comparison of the amounts of precipitation (Figure 6-3). A wash-out effect could also be observed at the sampling from 02/03/03 to 02/06/03 again at the monitoring station Taunus-Observatorium (Kleiner Feldberg) (Figure 6-4). After decreasing ambient temperatures during the sampling from 02/03/03 to 02/04/03 and a constant temperature of -5°C during the sampling from 02/04/03 to 02/05/03, the ambient temperature decreased again to -6°C during the sampling from 02/05/03 to 02/06/03. The first decrease of the measured MTBE concentration from 37 ng/L to 11 ng/L might therefore be due to a wash-out effect, whereas the reason for the subsequent increased concentration of 33 ng/L could probably be due to the decreasing temperature during the sampling from 02/05/03 to 02/06/03. The wind directions during the mentioned sampling events at the Taunus-Observatorium (Kleiner Feldberg) in February 2002 and in February 2003 varied in a narrow range between WSW-NW and W-NW, respectively. The wind speeds were only gentle breeze.

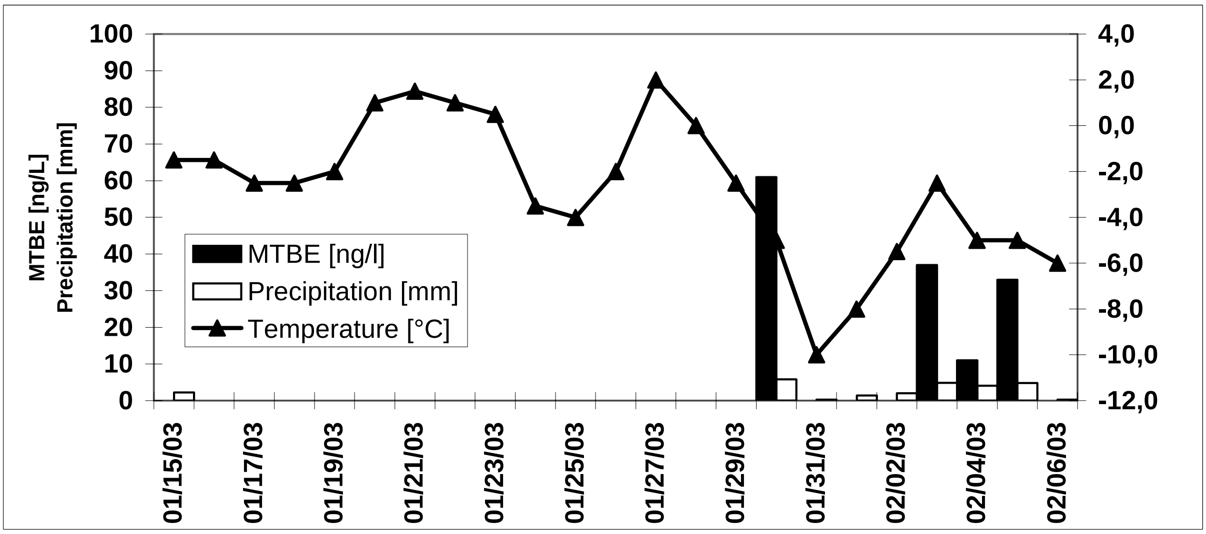

Figure 6-4: Measured MTBE concentrations in snow samples collected in January/February 2003 at the monitoring station Taunus-Observatorium (Kleiner Feldberg) versus ambient temperatures and amounts of precipitation. Note that the samples that are represented on 02/03/03, 02/04/03 and 02/05/02 were taken from 02/03/03-02/04/03, from 02/04/03-02/05/03 and from 02/05/03-02/06/03 respectively. Samples <10 ng/L were calculated as 10 ng/L. For single results see Appendix Table A5.

Considering the results obtained from samples from the Schauinsland and the Taunus-Observatorium (Kleiner Feldberg), the variation of MTBE snow concentrations found in this study can largely be explained by meteorological conditions like ambient temperatures and the time span between previous precipitation events and the actual time of sampling.

The mean (median) MTBE concentrations measured in urban and rural snow during the present study of 70 ng/L (54 ng/L) and 132 ng/L (78 ng/L) were about two (two) and nine (eight) times higher than those determined in rain precipitation (Achten *et al.*, 2001c). This indicates a high scavenging efficiency of snow with respect to MTBE. However, in order to obtain a detailed understanding of processes that are involved when MTBE or other organic pollutants are extracted from the atmosphere by snow, it is important to consider factors such as concurrent air sampling under well defined meteorological conditions as well as the characterization of the type of snowfall (Wania *et al.*, 1998; Franz and Eisenreich, 1998). The quantitative treatment of snow scavenging processes by using a model based on concepts that are applied for rain (i.e. the calculation of the total scavenging ratio W_T) (Wania *et al.*, 1998) revealed for hydrophobic organic chemicals only a low dissolution of pollutants in the above mentioned quasi-liquid layer. If the pollutants have high vapor pressures, vapor scavenging controls deposition, since in this case W_T is controlled by the product of snow area (m^2/m^3 melt water) and an interface-air partition coefficient. This coefficient is defined as the ratio of the equilibrium concentrations on the interface and the air phase, and describes the partitioning of the contaminant between the air phase and the water or ice surface. Its product with the snow area controlling W_T plays the same role as the dimensionless water-air partition coefficient, which is used to describe rain scavenging (Wania *et al.*, 1998). For volatile organic compounds with low affinity to particles like MTBE, vapor scavenging should be the dominating snow scavenging process. Even for some semi-volatile PCBs and PAHs, vapor scavenging was shown to be the dominating snow scavenging process rather than particle scavenging (Franz and Eisenreich, 1998; Wania *et al.*, 1999). A good approach to quantify the sorption of organic vapors to snow are the logarithmic sorption coefficients $\log K_{i\ \text{snow surface/air}}$, derived from IGC measurements at –6.8°C conducted by Roth *et al.* (2004). These sorption data are normalized to the surface area of the snow samples. The minimum value of the 60 compounds measured was calculated for n-octane ($\log K_{i\ \text{snow surface/air}} = -4.41$), aniline showed the maximum value of $\log K_{i\ \text{snow surface/air}} = -2.14$. The value for MTBE was $\log K_{i\ \text{snow surface/air}} = -3.80$. From the values of the 60 compounds measured, a predicting tool for the sorption of other organic compounds to snow was developed (Roth *et al.*, 2004). The sorption coefficient of MTBE was in the same range as the values of other ether oxygenates like *tert*-amyl methyl ether (TAME) ($\log K_{i\ \text{snow surface/air}} = -3.53$) and ethyl *tert*-butyl ether (ETBE) ($\log K_{i\ \text{snow surface/air}} = -3.63$). The sorption coefficients of the MTBE degradation products *tert*-butyl formate (TBF) ($\log K_{i\ \text{snow surface/air}} = -4.07$) and *tert*-butyl alcohol (TBA)

($\log K_{i\ \mathrm{snow\ surface/air}}$ = -2.40) were in the same range and one order of magnitude higher, respectively.

However, the physical and chemical properties of the ice surface and the processes that contribute to the sorption on ice still remain unclear. There is some evidence for a combination of different processes such as adsorption on the ice surface, adsorption on the QLL/air interface, and dissolution in the bulk ice or QLL. The fact that measured snow sorption coefficients and extrapolated water surface coefficients of polar organic compounds (MTBE: quotient 1.0) are in the same range at -6.8°C (Roth et al., 2004), may indicate sorption of MTBE to the ice surface as well as sorption to a QLL/subcooled liquid. The latter makes the temperature dependent Henry's law coefficient of MTBE even at temperatures below 0°C to an important sorption parameter. Grain boundaries, veins, nodes and defects in the ice lattice may also determine the sorption in or on the ice (Roth *et al.*, 2004). Detailed studies assigning the sorption of organic pollutants like MTBE or one of its atmospheric degradation products, TBA, on ice surfaces to these specific processes are required.

MTBE was shown to be a compound of relevance for drinking water, but despite the fact that emissions to air from the use of gasoline were proposed as the main source of MTBE to the environment (MEF, 2001), the MTBE input in river water via precipitation was shown to be only visible in small urban creeks (Achten *et al.*, 2002a). Most of the MTBE in rivers cannot originate from diffusive sources such as precipitation but has to be attributed to point sources. This is confirmed by the present study indicating that MTBE deposition from the atmosphere by snow to shallow groundwater and surface water in Germany can only contribute to slightly increased background concentrations.

6.5. Conclusions

In the present study, MTBE could be detected in 28 of 43 (65%) snow samples from 13 different locations. The concentrations ranged from 11 ng/L to the maximum concentration of 631 ng/L at the monitoring station Schmücke. Compared to formerly analysed rainwater samples, the MTBE amounts that were found in the collected snow samples were often higher (>100 ng/L). This confirms previous observations of other contaminants that show snow to be a more effective scavenger for organic contaminants than rain. Three snowpack samples taken at different locations within the city of Frankfurt/M had similar MTBE contents of 108-127 ng/L. Samples from rural and urban locations did not show significant differences in mean MTBE concentrations. Lower photochemical degradation of MTBE in winter, moving air masses and the ability of snow to significantly scavenge gas phase impurities from the atmosphere may explain the MTBE amounts that could be found even in the snow samples from rural and remote areas. A temperature dependency of the MTBE snow concentrations and a wash-out effect could be observed in samples from the monitoring stations Schauinsland and Taunus-Observatorium (Kleiner Feldberg). In future studies concurrent measurements of MTBE in air samples have to be included, which first requires the improvement of analytical methods to determine MTBE in the expected low concentration range in ambient air of rural areas.

7. COMPARISON OF MTBE CONCENTRATIONS IN GROUNDWATER OF URBAN AND NON-URBAN AREAS IN GERMANY

7.1. Abstract

The occurrence of the gasolione oxygenate methyl *tert*-butyl ether (MTBE) in groundwater samples from known benzene, toluene, xylene (BTEX) and/or hydrocarbon (HC) contaminated sites (n=29), non-urban (n=74) and urban sites (n=67) in Germany was investigated. The analyses revealed detection frequencies of 58% (contaminated sites), 24% (non-urban sites) and 63% (urban sites) at a detection limit of 10 ng/L. The detection frequencies using an assessment level of 5 micrograms per liter (µg/L) were 46%, 0% and 4%. Median (maximum) MTBE concentrations were calculated for non-urban and urban samples as 177 ng/L (2149 ng/L) and 57 ng/L (47 µg/L). The data from non-urban samples revealed MTBE detections mainly at public supply wells with high pumping rates. MTBE was more frequently detected in urban samples, most probably due to the higher atmospheric input. Higher concentrations above 1 µg/L in urban areas were found in wells located at industrial sites, where also a MTBE plume was accidentally detected during the study. The results of the present study were comparable to other studies investigating MTBE in groundwater in Germany. The comparison with U.S. data on MTBE in groundwater using an assessment level of 0.2 µg/L revealed a higher overall median MTBE concentration in the groundwater samples from Germany collected during the present study of 1.21 µg/L, compared to 0.67 µg/L determined in the U.S. Both values were determined without data from known contaminated sites. However, the overall median value in Germany of 0.097 µg/L based on the detection limit of 10 ng/L was significantly lower.

7.2. Introduction

Methyl *tert*-butyl ether (MTBE) is an oxygenate and mainly used as a fuel additive to enhance the octane number and to reduce air pollution. About 20 million tons (t) are used worldwide mainly for this purpose. The production capacity of MTBE in Europe today is about 3 million t and approximately equal to the annual demand (EOFA, 2003). In Germany, about 683,900 t (Sur *et al.*, 2003) were consumed in the year 2001. If MTBE is released into the aquatic environment, it may affect drinking water sources. MTBE has some physico-chemical properties that enable it to migrate long distances within the groundwater at almost the same velocities as those of the recharge water (Squillace *et al.*, 1996b). In addition, it has a low aesthetic level of 5 micrograms per liter (µg/L), California's secondary Maximum Contaminant Level (MCL) (Williams, 2001). These properties and its occurrence in the aquatic environment (Squillace *et al.*, 1996b; MEF, 2001; Moran *et al.*, 2004) have led to concern in the USA and Europe because of its potential threat for drinking water sources (MEF, 2001; Clawges *et al.*, 2001; Grady, 2003). MTBE in drinking water may cause possible human health effects (Moran *et al.*, 2004). In the U.S., its overall detection frequency of 7.6% in groundwater, drinking water sources and drinking water is comparable to those of other volatile organic compounds (VOCs) such as trichloroethene (TCE) and tetrachloroethene (PCE), which are being used as solvents since a long time (Moran *et al.*, 2004).

MTBE can reach the (shallow) groundwater via point and non-point sources. The atmosphere as non-point source for MTBE in shallow (urban) groundwater or surface water was described in several studies (Pankow *et al.*, 1997; Baehr *et al.*, 1999a; Baehr *et al.*, 1999b; Bender *et al.*, 2000; Baehr *et al.*, 2001). MTBE detections in groundwater may be attributed to atmospheric deposition, since MTBE persists in the atmosphere at concentrations implying detectable aqueous-phase equilibrium concentrations (Baehr *et al.*, 1999b; Achten *et al.*, 2001c) and MTBE seems not to be degraded below detection limits of 0.1 µg/L and less in the unsaturated zone (Baehr *et al.*, 1999b). Although the resulting groundwater concentrations of atmospheric MTBE deposition might be low, the latter source should not be neglected, since emissions to air from the use of gasoline have been proposed to be the main source of MTBE releases to the environment (MEF, 2001). Leaking above-ground and underground storage tanks at tank farms, refineries or gas stations and accidental spills are typical point sources (Squillace *et al.*, 1996b) that can cause MTBE contaminations in the groundwater to reach levels of concern, which are above the known taste and odor thresholds of 5-40 µg/L. Sources that include point and non-point MTBE releases are (urban) stormwater runoff and motorized watercraft. The latter is primarily important for MTBE releases into river and surface water. Studies on the behavior of MTBE during riverbank filtration have shown that MTBE may also reach groundwater by the infiltration of surface water into aquifers (Achten *et al.*, 2002b; Sacher, 2002). Lake/well interactions may complicate investigations on the occurrence of MTBE in groundwater (Baehr *et al.*, 1999a). Further sources for MTBE in river water are municipal and industrial sewage plants (Achten *et al.*, 2002a; Kolb *et al.*, 2003). Possible MTBE releases into groundwater from industrial sites apart from petrochemical sites have only been investigated in part (Blankenhorn, 2002), probably because only 1.5% of the MTBE produced was used for industrial purposes in the year 1997 in Europe (MEF, 2001).

In the U.S., large amounts of data on the occurrence of MTBE in groundwater and source water were obtained by studies conducted during the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program and associated programs from other organizations (Squillace *et al.*, 1996a; Bruce *et al.*, 1996; Moran *et al.*, 2004). Although in the meantime there now exists MTBE data from precipitation (Achten *et al.*, 2001c; Stockerl, 2002), river water (Achten *et al.*, 2002a; Sacher, 2002) and groundwater (Effenberger *et al.*, 2001a; Klinger *et al.*, 2002; Stockerl, 2002; Sur *et al.*, 2003) in Germany and Europe (MEF, 2001), there is still a lack of data regarding German groundwater (Klinger *et al.*, 2002). In particular, the widespread prevalence of MTBE remains unclear. MTBE measurements in areas without known contaminations would be useful to better understand the diffusive MTBE input and to recognize whether there are potential threats to drinking water supplies, in addition to contaminated sites. The data might also be useful for modeling the long-term effects of MTBE releases into the aquatic environment. The objective of the present study therefore was to collect MTBE groundwater data from known contaminated sites as well as from urban and non-urban areas in Germany in order to obtain patterns that could be compared to other MTBE studies and the implications that were made therein. The urban sampling included some sites where past or present industrial activities are located in the vicinity.

7.3. Experimental

7.3.1. Contaminated Sites

Seven sites with known benzene, toluene, xylene (BTEX) and/or hydrocarbon (HC) contaminations or sites with wells close to BTEX/HC contaminations were investigated from April 2000 to September 2001 to establish the (co-)occurrence of MTBE. With the exception of one site, all investigated sites are located in the city of Düsseldorf in the federal state of North Rhine-Westphalia. The BTEX/HC contaminations at the different sites were all caused by accidents or leaking storage tanks at gas stations. One site in Düsseldorf was recently described elsewhere by Forner *et al.* (2003).The shallow groundwater samples (n=29) collected at 26 wells were obtained approximately 2-18 m below land surface. Two wells in Düsseldorf could be sampled at two and three different well depths, since these wells had screened intervals.

7.3.2. Non-Urban Samples

Non-urban groundwater samples (n=74) were taken from November 2000 to May 2003 at 55 different wells in the rural district of Main-Kinzig in the federal state of Hesse, except one sample which was collected at an agricultural ground in Baden-Württemberg. The sampling consisted mainly of public supply wells in water protection areas and monitoring wells that are hydraulically connected to the public supply wells. Only two samples originated from wells that are not located within a water protection area. Two of the water protection areas are characterized by anthropogenic activities, e.g. highways, agriculture or, in one case, a gas station located in the extended protection area. The samples included shallow groundwater obtained from approximately 5-10 m below land surface as well as groundwater from deeper aquifers obtained from approximately 20-90 m below the ground. Four samples were collected in the protection area of spas and were taken from depths down to 538 m below land surface.

7.3.3. Urban Samples

Urban groundwater samples (n=67) were collected from November 1999 to March 2002 in the Rhine-Main area in Hesse around Frankfurt/M (n=33) at 19 different wells. 34 samples taken in February 2002 and August 2002 from 33 wells originated from a city named City 1 herein. The wells that were sampled in the Rhine-Main area are under the influence of different anthropogenic activities and possible MTBE sources. 20 samples from 6 wells collected in this area consisted of groundwater probably influenced by the river Main and the small river Nidda (1 well) via riverbank filtration. The remaining samples from the Rhine-Main area (n=13) were possibly influenced either by industrial or by vehicle activities. The same conditions could be found at the sampling sites in City 1. Nearly all of the wells in City 1 were in the vicinity of motorways and most of the samples originated from wells in areas with past or present industrial activities.

The urban samples consisted primarily of shallow urban groundwater obtained from approximately 3-12 m below land surface. Three samples in City 1 were collected from deeper aquifers, two of them represented sources of drinking water. The third sample was collected at one of two wells that allowed sampling at different depths. It should be noted that the classification of the investigated wells, i.e. the land use categories urban and non-urban, could not be compared to digital data on population density, like for example in the U.S. 12-state drinking water survey on MTBE (Grady and Casey, 2001). Although there was available data including population densities from cities and districts where the samples were taken, this parameter, that usually classifies the ambience of a well (Moran *et al.*, 1999; Moran *et al.*, 2004), was omitted in some cases. The ambient conditions that were found when a well was sampled led in those cases to a classification different from the one obtained from available geospatial data.

7.3.4. Sampling and Analysis

The groundwater samples were taken 2-3 m below the water table by using mobile pumping stations. After a period of pumping, the samples were collected when the field parameters (e.g. conductivity, pH) showed constant values or when the water within the tube of the well was replaced three times. When drinking water wells were sampled, water taps in the waterworks were used sometimes. The samples were stored in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. They were stored and transported at 4°C and analyzed within three weeks. During sampling and transport always field blanks were present and analyzed parallel to the samples. The analysis was performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS). Mass chromatography of m/z 73 (MTBE) and m/z 76 (internal standard d_3MTBE) was used for quantitation. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. The detection limit was 10 ng/L with a relative standard deviation of 11%. Laboratory blanks were regularly measured. A detailed description of the analytical method is published elsewhere (Achten *et al.*, 2001b), except that a J&W Scientific DB-624 column (60 m x 0,32 mm) with a film thickness of 1.8 µm was used as chromatographic column.

The detection frequencies were calculated by classifying a well as positive if one sample contained detectable MTBE concentrations. Median MTBE concentrations were calculated without samples below the detection limit. Assessment levels of 1 and 5 µg/L were used to make the data more comparable. The 5 µg/L concentration is California's secondary MCL (maximum contaminant level) (aesthetic-based) for MTBE.

7.4. Results and Discussion

7.4.1. Contaminated sites

MTBE occurred at least in one well in each case at six of the seven investigated sites. MTBE concentrations above 5 µg/L were measured at four sites. The maximum concentration of 42 mg/L was detected in groundwater of a treatment well in the subsurface of a gas station. Three investigated monitoring wells are also located on the terrain of this gas station. Upstream of the treatment well, at a distance of 14 m, only 263 ng/L were measured in the monitoring well, whereas the monitoring wells at the sidestream of the treatment well at distances of 25 m and 15 m revealed concentrations of 100 µg/L and 5 µg/L, respectively. Downstream of the treatment well 210 µg/L were measured by the remediation company at a distance of about 11 m. The source of MTBE are releases of gasoline into the subsurface that occurred in the past. After treatment of the contaminated aquifer to remove HC, BTEX and polycyclic aromatic hydrocarbons (PAHs), groundwater monitoring was carried out regularly. Since 2001, the monitoring also included MTBE. The monitoring results from 2001 including the MTBE measurements within the present study led to renewed treatment measures. The treatment, which consists of pumping and treating with activated carbon, as well as the hydrogeological conditions at the affected site, prevent the horizontal and vertical migration of the contaminants away from the gas station.

At one site in Düsseldorf MTBE concentrations of 62 µg/L, 12 µg/L and 2 µg/L were measured in monitoring wells downstream of a gas station during the present study in the year 2000. The results of detailed monitoring and hydrogeological investigations in the years 2002/2003 conducted at this site (Forner *et al.*, 2003) suggest that MTBE originally comes from an oil separator, by leaking temporarily into the aquifer. Within the aquifer, MTBE is distributed in a vertical concentration profile influenced by the groundwater flow direction. There are indications that the plume might be diluted and migrate further downstream (Forner *et al.*, 2003).

The results obtained throughout the sampling at the remaining contaminated sites revealed MTBE concentrations in the range of 56 ng/L-37 µg/L and the contaminations are most probably due to releases from the vicinal gas stations. The detection frequency in groundwater from BTEX/HC contaminated sites was 58% and at assessment levels of 1 µg/L and 5 µg/L it was still 46% (Figure 7-1). The median and maximum concentrations found at the contaminated sites were 1400 ng/L and 42 mg/L, respectively (Figure 7-2). These results are comparable to a study conducted by Effenberger *et al.* (2001a), where MTBE could be found at five of ten investigated gasoline contaminated sites in Germany at concentrations above 20 µg/L. The results of the present study are also comparable to the investigation of the effects of gasoline formulation on MTBE contaminations in private wells located in New York State near gasoline stations (Lince *et al.*, 2001). In this study, MTBE was detected in 28% of the wells situated close to gas stations (<0.8 km). The higher value of 46% in the present study is most probably due to the biased sampling towards gas stations with known contaminations. Nevertheless, the findings of the present study support the supposition that there are sites with MTBE subsurface contaminations where MTBE still remained undetected (Effenberger *et al.*, 2001a). Past releases of MTBE may pose a risk to drinking water supply wells in the future (Johnson *et al.*, 2000) due to the persistent behavior of MTBE in the subsurface.

7.4.2. Non-Urban Samples

MTBE was detected in 13 of 55 (24%) wells sampled in non-urban areas. The detection frequency at an assessment level of 1 µg/L was 5% (Figure 7-1). None of the samples contained MTBE at concentrations higher than 5 µg/L. The median concentration was 177 ng/L (Figure 7-2). These low concentrations are due to the predominant sampling at water protection areas.

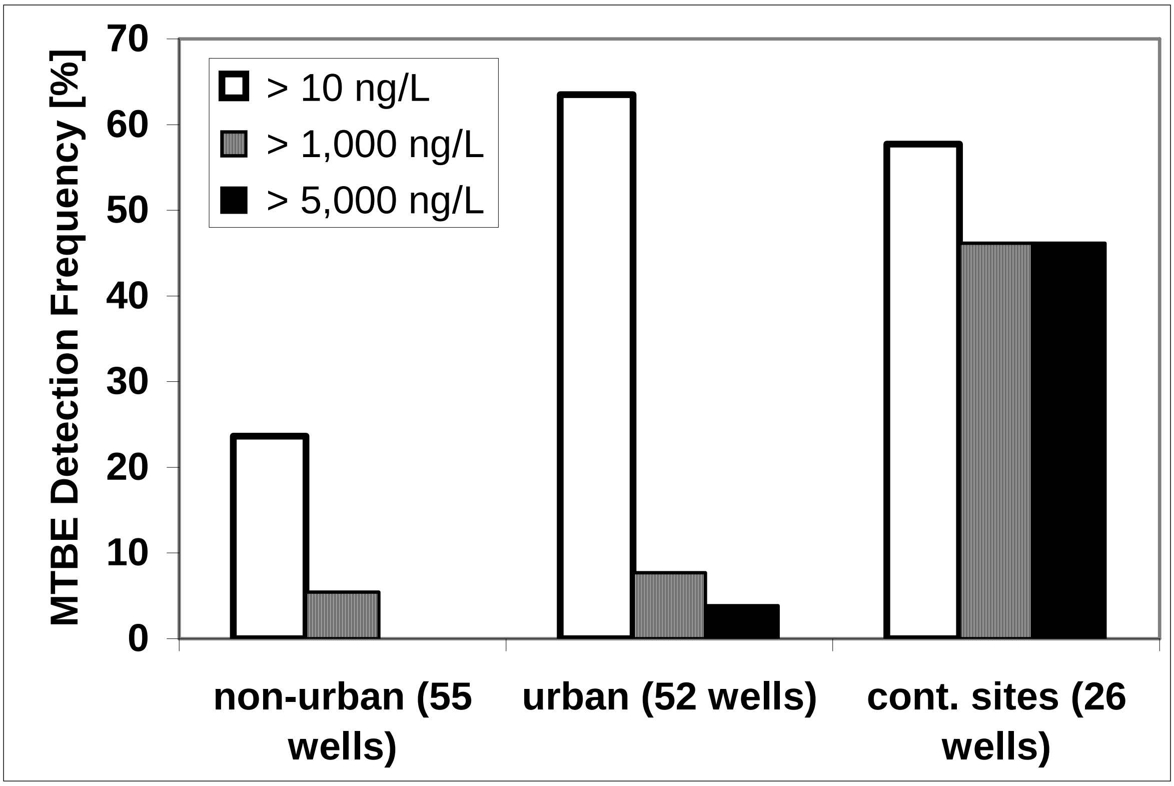

Figure 7-1: Detection frequencies of MTBE in non-urban wells, urban wells and wells at known contaminated sites. Method detection limit was 10 ng/L with a relative standard deviation of 11%. For single results see Appendix Table A6-A8.

In November/December 2000, two drinking water wells and one monitoring well located within one of the investigated water protection areas showed MTBE concentrations ranging from 629 ng/L (monitoring well), to 1735 ng/L (drinking water well) and up to the maximum concentration measured in non-urban samples of 2149 ng/L (drinking water well).

Subsequent re-sampling at the two drinking water wells in February 2001, November 2002 and May 2003 revealed maximum MTBE concentrations of 34 ng/L, 12 ng/L and <10 ng/L, respectively. MTBE was not detectable in the only sample subsequently taken from the monitoring well in February 2001. The source of the MTBE that was detected in these wells and the variations during the sampling period remained unclear. A motorway and a gas station can be found within the extended water protection area. In February 2001, a MTBE concentration of 628 ng/L could be measured in a monitoring well located at the gas station. Although the water of the two drinking water wells mainly originates from deeper aquifers, the high pumping rates in these public supply wells may lead to a significant proportion of water that may have intercepted the areas of high traffic density or possible point sources (Baehr *et al.*, 1999a).

Similar realtionships may have caused the positive MTBE detections in four drinking water wells in a second investigated water protection area. In the period from February 2001 to May 2003, MTBE could be detected in 3 of 4 drinking water wells at concentrations in the range of 105-377 ng/L, 120-800 ng/L and 1207-1593 ng/L, respectively. In February 2001, water from the collector well and input/output water of the elevated tank also was analyzed for MTBE. The elevated tank and the collector well are supplied by two of the drinking water wells with positive MTBE detections and the one where MTBE was not detectable. The input, output and collector well water showed MTBE concentrations of 131 ng/L, 117 ng/L and 75 ng/L, respectively. These concentrations reflected the mixture of the three supply wells. In addition to the different possible sources, i.e. a gliderport, motorways and anthropogenic activities in the extended water protection area, the location of the wells within the area of a floodplain creates difficulties to determine the origin of the MTBE found in the drinking water wells. The groundwater table is strongly influenced by the receiving stream Kinzig; an infiltration of surface water containing possible contaminants cannot be ruled out. Interactions between surface water and groundwater can complicate groundwater investigations on MTBE (Baehr *et al.*, 1999a) and MTBE was shown to reach drinking water sources via river bank filtration (Sacher, 2002; Achten *et al.*, 2002b).

In the remaining non-urban samples (n=24), including additional samples from other water protection areas, MTBE was only detectable in two samples at concentrations of 99 ng/L and 177 ng/L, respectively. These low concentrations may be due to diffusive MTBE inputs, mainly via precipitation. A few studies have investigated the atmosphere as diffusive MTBE source in shallow groundwater by sampling and in a few cases by modeling the processes in air, rainfall, snow, unsaturated zone gas, urban streams and shallow groundwater (Pankow *et al.*, 1997; Baehr *et al.*, 1999a; Baehr *et al.*, 1999b; Bender *et al.*, 2000; Baehr *et al.*, 2001; Achten *et al.*, 2001c).

MTBE input from the atmosphere in New Jersey via precipitation was shown to be high enough to cause detection in shallow groundwater of 100 ng/L (Baehr *et al.*, 1999b). If the associated stormwater runoff, e.g. from motorways crossing the investigated area, is also attributed to the diffusive source atmosphere/precipitation, then values from 1-5 µg/L may be suitable to distinguish between point sources and diffusive sources (Schmidt *et al.*, 2003). Nevertheless, some uncertainty remains due to possible superimpositions of point and non-point MTBE sources and due to the variables that lead to detection/non-detection of MTBE in shallow groundwater. Distinguishing between point and non-point sources is critical, since atmospheric VOC concentrations in groundwater originating from the atmosphere are expected to remain at a low level, in contrast to groundwater contaminations from VOCs originating from point sources, that may increase over time (Baehr *et al.*, 1999b). Point sources like leaking underground storage tanks or accidental spills cause stable or moving MTBE plumes that are expected to migrate longer distances than other gasoline constituents (e.g. benzene) (Stocking *et al.*, 1999). This limits the possibility to distinguish between point and non-point sources via co-occurrence of other gasoline constituents (Bruce and McMahon, 1996). During advective transport in groundwater, dispersion and dilution lead to low MTBE concentrations, suggesting diffusive input, although the detected MTBE originates from a point source. If MTBE in shallow groundwater originates from non-atmospheric sources, outgasing from the aquifer is possible and can be observed (Baehr *et al.*, 2001) and used to determine the origin (atmospheric or non-atmospheric) of the MTBE.

The vulnerability of aquifers to (low) MTBE concentrations is influenced by an interaction of anthropogenic and hydrogeologic variables. Anthropogenic factors like population density and MTBE use in gasoline influence the input of MTBE into the hydrologic cycle, whereas hydrogeology determines transport and fate (Moran *et al.*, 2004). Hydrogeologic variables that were shown to be more or less significant correlated with the occurrence of MTBE in groundwater are recharge (more), aquifer consolidation (less) and soil permeability (less) (Moran *et al.*, 2004). Particularly the unsaturated zone processes seem to strongly influence the probability to detect MTBE in shallow groundwater. Results of Baehr *et al.* (1999b) from investigations in an aquifer suggest that variations in recharge and unsaturated zone thickness may be associated with the probability of detecting MTBE in shallow groundwater. If MTBE reaches the unsaturated zone within a non-aqueous phase liquid (e.g. gasoline), vapor diffusion seems to be the major pathway to reach the groundwater (Stocking *et al.*, 1999; Dakhel *et al.*, 2003), whereas in the case of recharge and input via precipitation the transport is advection-dominated (Baehr *et al.*, 2001). MTBE degradation was observed in the unsaturated zone with a half-life from a few months to a couple of years (Baehr *et al.* 2001) and evapotranspiration also plays a role in terms of VOC transport to groundwater, at least in semiarid locations (Johnson *et al.*, 2003). The interaction of these anthropogenic/hydrogeologic factors may explain some detections/non-detections and concentrations of MTBE in the non-urban samples as well as in the below discussed urban groundwater samples.

7.4.3. Urban Samples

The detection frequency in urban wells was 63%, i.e. in 33 of 52 wells or different well depths MTBE could be detected at concentrations above 10 ng/L. At an assessment level of 1 and 5 µg/L, the detection frequencies were 8% and 4%, respectively (Figure 7-1). Although the median concentration of 57 ng/L is lower than the median concentration in non-urban samples, the maximum concentration (47 µg/L) as well as the detection frequencies (Figures 7-1, 7-2) clearly indicate the higher probability to detect MTBE in shallow urban groundwater than in non-urban samples, due to the higher population density and thus higher use of gasoline.

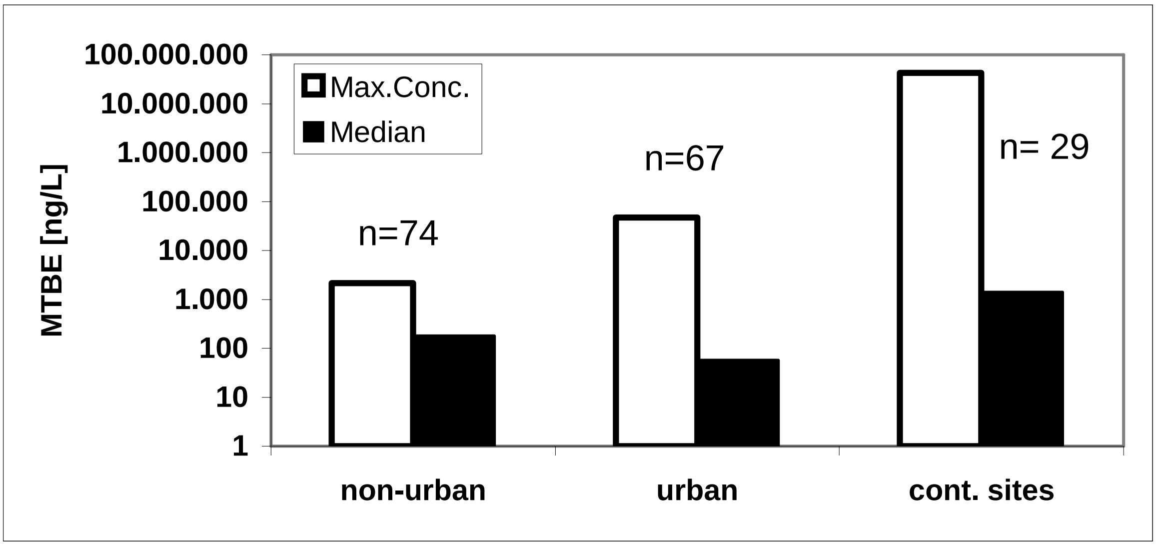

Figure 7-2: Maximum and median MTBE concentrations in samples from non-urban wells, urban wells and wells at known contaminated sites (n=number of samples). Method detection limit was 10 ng/L with a relative standard deviation of 11%. Note the logarithmic scale. For single results see Appendix Table A6-A8.

During the first sampling campaign in City 1 in February 2002, the MTBE concentrations that were found in 13 of 25 samples were all below 100 ng/L, except one sample with 8 µg/L.

Except one drinking water sample from a deep aquifer below 100 m, the samples were taken from wells at locations possibly influenced by past or present industrial activities and vehicle traffic. The low concentrations most probably indicate only diffusive sources like atmospheric input without point sources in the subsurface. The second sampling consisted of the well where during the first sampling 8 μg/L MTBE could be detected and vicinal wells at distances below 750 m. Except two wells, the concentrations detected within this second sample collection ranged between 71 and 118 ng/L. These low concentrations did not allow to associate the occurrence of MTBE in these wells with the contaminated well from the first sampling. In the re-sampled well 6 μg/L could be measured on this occasion, whereas in a multilevel well about 310 m downstream of this well MTBE could be detected at concentrations of 47 μg/L in the shallow groundwater and 276 ng/L in the deeper aquifer. This indicated a possible MTBE plume that migrates not only horizontally, but also to a certain extent vertically, even into deeper aquifers, due to the extensive use of the deeper aquifers for drinking water supply. The source of the plume remained unclear, since industrial plants, a gas station and a small tank farm could all be considered as possible sources. The drinking water provided for City 1 has not been to date affected by this plume.

In the 13 wells that were sampled in the Rhine-Main area at locations where industrial or vehicular activities are present, MTBE could be detected in 11 wells at concentrations in the range of 22-2356 ng/L. Only two wells exceeded 1 μg/L and they are both situated in industrial areas. The results and implications of the main part of the 20 samples from 6 wells that were taken in the vicinity of the rivers Main and Nidda have been discussed elsewhere (Achten *et al.*, 2002b). MTBE was detectable in all wells at concentrations from 12-250 ng/L, except three wells including the well influenced by the small river Nidda.

The more frequent detection of MTBE in urban areas than in non-urban areas was comparable to the results of Klinger *et al.* (2002), where 80 urban and 90 rural wells in Germany were sampled. At a limit of determination of 50 ng/L, MTBE was detected in 9% of the rural wells and 49% of the urban wells. Similar to the present study, MTBE occurred in urban and rural wells above 5 μg/L only in 4% and 0%, respectively. Klinger *et al.* (2002) also detected sites in urban areas where MTBE occurred at high concentrations in the μg/L-range most probably originating from point sources, like the plume that was found in City 1 in the present study. This plume and the two wells in the Rhine-Main area that exceeded 1 μg/L are located in industrial areas. 1.5% of the MTBE consumed in Europe in 1997 was used in industrial plants (MEF, 2001). Industrial MTBE releases are important sources of MTBE in German rivers (Achten *et al.*, 2002a; Kolb *et* *al.*, 2003) and the occurrence of MTBE at industrial sites (apart from petrochemical sites) is still to be investigated in future studies. Although the sampling in the present study included such locations, it was not possible within the scope of this study to determine whether increased MTBE concentrations originated from industrial MTBE releases in the past or from spills and leaks at gas stations that were also present nearby. MTBE was also positively detected at concentrations of 200-600 ng/L at industrial sites by the Landesanstalt für Umweltschutz Baden-Württemberg in the year 2001 (Blankenhorn, 2002).

The general high MTBE detection frequencies compared to non-urban samples and the overall low MTBE concentrations in shallow urban groundwater in Germany measured in the present study and by Klinger *et al.* (2002) suggest the urban atmosphere as an important source of MTBE in shallow urban groundwater, but the above mentioned superimpositions of sources should be kept in mind. Urban air in Europe was shown to contain mean MTBE concentrations from 0.9 $\mu g/m^3$ – 2.8 $\mu g/m^3$, whereas at rural locations MTBE air concentrations ranged from 0.146 $\mu g/m^3$ – 0.78 $\mu g/m^3$ in recent studies (Achten *et al.*, 2001c; Hellen *et al.*, 2002; UMEG, 2002). The investigation of precipitation sampled throughout Germany revealed similar patterns, since MTBE was more often detectable in urban (86%) than in rural (18%) samples (Achten *et al.*, 2001c). However, the uptake of gasoline contaminants from small spills at motorways or gas stations into urban stormwater as possible second or main MTBE source has to be considered as it plays a more important role than in non-urban areas: MTBE in stormwater in the U.S. could be associated with the type of urban land surfaces (Lopes and Bender, 1998), the average percent of impervious surface possibly correlates with MTBE concentrations (Lopes and Bender, 1998) and higher MTBE concentrations could be associated with runoff from gas stations (Borden *et al.*, 2002). Nevertheless, urban air is potentially an important source of MTBE in urban waters because the detection frequencies in stormwater in the U.S. reflected seasonal MTBE use (Lopes and Bender, 1998). The average percent of sealed surface and the percentage of water that reaches the shallow groundwater without entering the sewerage should determine the occurrence of MTBE in urban groundwater samples at concentrations below 1-5 µg/L.

7.4.4. Comparison of MTBE Data in Germany and the USA

The results of urban and non-urban samples (except the contaminated sites) in the present study combined with the results from other groundwater monitoring programs in Germany (Klinger *et al.*, 2002; Stockerl, 2002; Sur *et al.*, 2003) were compared to U.S. groundwater data. Similar to the German studies, the wells sampled within the U.S. NAWQA occurrence studies (Moran *et al.*, 2004) were not located in the vicinity of known point source releases. But there are also some differences between the German and the U.S. studies. The German studies consisted of a total of 195 urban and 293 non-urban wells, whereas the U.S. study consisted of 1,593 urban samples and 2,309 non-urban samples. Furthermore the U.S. samples from urban and non-urban areas were divided into the categories of high and low MTBE use areas, since the influence of the MTBE use in gasoline was shown to be more important than population density (Moran *et al.*, 2004). High MTBE use areas were defined as areas that were either designated for reformulated gasoline (RFG) usage or where the long-term average MTBE content in gasoline was greater or equal to 3% v/v (Moran *et al.*, 2004). The average MTBE content of about 1.5% v/v in German gasoline is the same all year round and no area specific contents are designated. It should be noted that Eurosuper, with 64% of the sales volume the mostly sold gasoline in Germany in 2001, contains about 3% v/v MTBE (Sur *et al.*, 2003). Therefore, the results of the German samples may be classified between the U.S. high and low MTBE use categories (Figure 7-3). The anthropogenic data of the areas and the hydrogeologic data of the wells where the samples were taken in the NAWQA study were integrated within the evaluation when necessary, and the wells were unbiased and randomly chosen. In contrast to this, information about the investigated wells in Germany was in part rare, could not be published or remained unpublished. The well types that were sampled in the different studies also play an important role, e.g. due to the high pumping rates in public supply wells (Baehr *et al.*, 1999a; Moran *et al.*, 2004).

Although these differences have to be kept in mind, the comparison of detection frequencies using no assessment level showed some interesting details. The ratios of detection frequencies between urban and non-urban areas in U.S. high MTBE use areas (3.0) and Germany (2.9) are comparable (Figure 7-3). This indicates that, similar to the U.S., the probability of detecting MTBE in groundwater was clearly related to population density, when controlling for MTBE use (Moran *et al.*, 2004). The detection frequencies of MTBE in urban and rural groundwater samples were higher in Germany than in the corresponding U.S. high and low MTBE use areas. The probability of detecting MTBE in groundwater in German non-urban samples was even higher than in urban samples from U.S. low MTBE use areas (Figure 7-3). The higher detection frequencies in the German groundwater samples might be due to the above mentioned differences within the study designs or due to the different limits of detections used within the German studies and the U.S. study. It also has to be kept in mind that the German urban data included some wells close to industrial sites. Nevertheless, the different detection frequencies may also reflect the different theoretical MTBE loads in Germany and in the U.S. If the areas of 9.36 million km^2 for the U.S. and 0.36 million km^2 for Germany are given and an amount of 12 million t and 0.683 million t of MTBE in the U.S. (Schmidt *et al.*, 2001) and in Germany (Sur *et *al.*, 2003) are used, the theoretical MTBE loads are 1.28 t/km^2 and 1.89 t/km^2 in the U.S. and Germany, respectively. The main monitoring variables that are theoretically affected by different MTBE loads will probably be the median concentrations obtained in the different study areas.

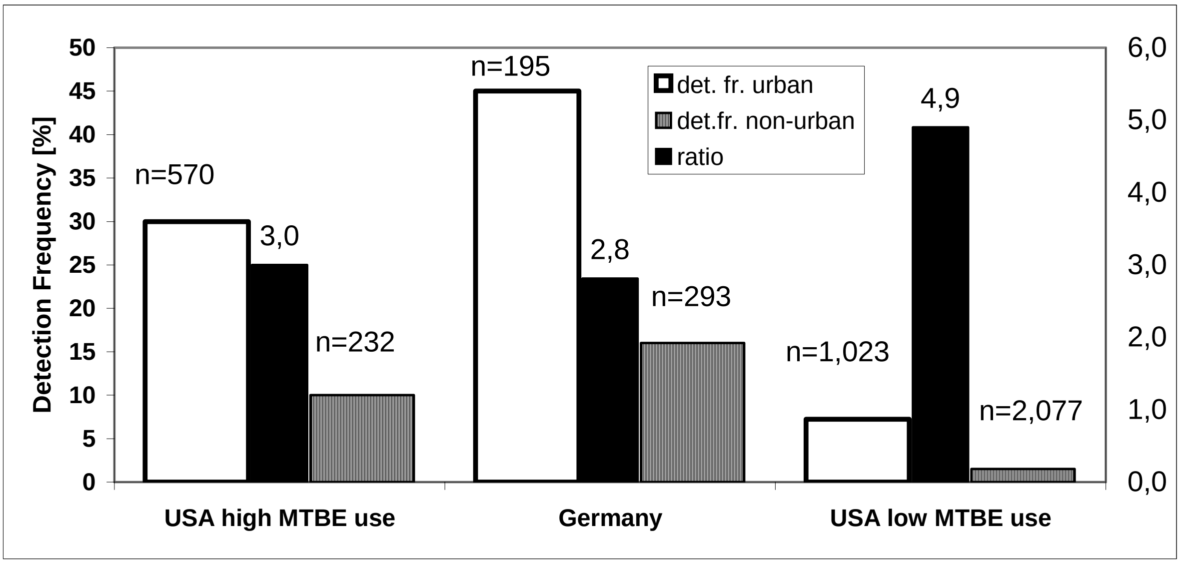

Figure 7-3: Comparison of MTBE detection frequencies at urban and non-urban areas in U.S. high and low MTBE use areas and Germany. The detection frequencies were calculated using no assessment level (n=number of samples/wells). The columns in the middle represent the ratios of urban to non-urban detection frequencies. Data sources are: U.S.: Moran et al., (2004). Germany: Klinger et al., 2002; Stockerl et al., 2002; Sur et al., 2003 and the present study. For single results of the present study see Appendix Table A6-A8.

The published median concentration in urban areas was higher in the U.S. at 0.5 µg/L (Klinger *et al.*, 2002) compared to the median values in Germany of 0.057 µg/L (this study) and 0.17 µg/L calculated by Klinger *et al.* (2002). The comparison of median values obtained from all detected MTBE concentrations (without data from known contaminated sites) within the present study with the median values from the U.S. NAWQA study revealed a lower median concentration in Germany of 0.097 µg/L to 0.67 µg/L in the U.S. The U.S. value was calculated using an assessment level of 0.2 µg/L (Moran *et al.*, 2004). By using this same level for the calculation in the present study, a median concentration of 1.21 µg/L was obtained. The ratio of these two median concentrations (1.21µg/L and 0.67 µg/L) and the ratio of the theoretical MTBE loads result in a 1.8-fold higher median MTBE concentration in German groundwater, reflecting a 1.5-

fold higher theoretical MTBE load. The higher median concentrations may subsequently influence the probability to find MTBE contents in groundwater above the detection limits.

7.5. Conclusions

According to the results of the present study it can be concluded that MTBE in shallow groundwater in Germany is ubiquitary at concentrations below 1-5 µg/L at least in urban areas. Its prevalence and concentrations in shallow aquifers are comparable to those in the U.S. Slightly higher detection frequencies in Germany might be caused by either the differences in the study designs or a higher theoretical MTBE load. As expected, and similar to the U.S., MTBE was more frequently detectable in urban areas, but concentrations above 1µg/L could be found even in non-urban drinking water wells located in water protection areas, probably caused by the high pumping rates in the selected drinking water wells.

The MTBE input into the shallow groundwater is determined by anthropogenic factors and the identification of the sources is difficult since different point and diffusive sources may be superimposed. Additionally, the different hydrogeologic variables influencing the fate of MTBE in the hydrologic cycle complicate the investigation of long-term effects of diffusive and punctual MTBE releases into the groundwater. Nevertheless, a concentration range of 1-5 µg/L seems to be useful as precautionary value (Schmidt *et al.*, 2003) when drinking water may be affected by MTBE contaminations. The comparison of the investigation of wells without known BTEX/HC contaminations and wells at contaminated sites associated with gas stations clearly indicated that the possible threat that MTBE poses to groundwater and drinking water supplies is mainly related to accidents during storage and distribution of gasoline. In addition to the MTBE occurrence at the sites with known HC/BTEX contaminations, the detected plume in City 1 shows that there might be many MTBE contaminated sites in Germany, probably also at industrial sites, which are undetected so far. However, the standards of UST constructions in the EU and the higher costs of gasoline within the EU compared to the U.S. are seen, respectively, as a preventive measure and factor against widespread serious groundwater contamination (Env.Exp., 2001; Sur *et al.*, 2003).

8. MTBE IN THE RIVER MAIN (GERMANY) - INVESTIGATION OF DIFFERENT SOURCES.

8.1. Abstract

The present study provides results from the monitoring of long-term methyl *tert*-butyl ether (MTBE) presence in Main water in Frankfurt am Main (Frankfurt/M) from the year 1999 to 2003. The data are compared to the MTBE amounts in representative water samples from possible MTBE release sources, i.e. precipitation sampled in Frankfurt/M and industrial/municipal sewage plant effluents. The results should contribute to the understanding of the influence of these three sources on the occurrence of MTBE in river water. MTBE could be detected in the river Main at the monitoring point at median (mean) concentrations of 66 ng/L (125 ng/L) (n=67). MTBE was detectable in 60% of the precipitation samples (n=89) at a median (mean) concentration of 30 ng/L (36 ng/L). Given the median values in precipitation and the river Main it could be concluded that only background concentrations of MTBE in the investigated Main water samples of up to 30 ng/L may be assigned to the direct atmospheric input. The concentration of 30 ng/L most probably represents a maximum value, since the precipitation data are based on monitoring results from the metropolitan area of Frankfurt/M. The comparison of the results of the investigations on industrial (n=34) and sewage plant effluents (n=66) and the MTBE contents in the river Main indicated that the largest source of MTBE in the river Main water are industrial effluents and that the second largest are sewage plant effluents including urban runoff. MTBE concentrations of up to 28 micrograms per liter (µg/L) were detected at three industrial effluents. The varying concentrations at different sampling dates in these outfalls show them as discontinuous point sources. Median (mean) MTBE concentrations of 49 ng/L (329 ng/L), 92 ng/L (271 ng/L) and 55 ng/L (81 ng/L) were detected in the remaining industrial effluents and the effluents of two municipal sewage plants. It could be concluded that such effluents contribute to increased background concentrations of MTBE in rivers such as the Main, since these concentrations are in the range of median and mean Main water MTBE concentrations. Elimination rates of 50% and 38% were calculated for the two municipal sewage plants. The theoretical loadings were determined at 9-14 kg/a and 2 kg/a.

Detailed sampling of Main water upstream and downstream of the outfall of a sewage plant was carried out in order to obtain quantitative results regarding the contribution of sewage plant effluents to the MTBE amounts in the river Main. The maximum contribution was calculated at 9% during four sampling events. This contribution may increase during heavy precipitation events or at industrial sites.

8.2. Introduction

The annual consumption of the oxygenate methyl *tert*-butyl ether (MTBE) in Europe increased by 23% between the years 1995-1999 (MEF, 2001). Annual demand of about 3 million tons (t) equals approximately the production capacity in Europe (EFOA, 2003). MTBE is mainly used as gasoline oxygenate to reduce exhaust emissions of carbon monoxide and to enhance the octane number in gasoline. In Germany, its usage was about 683,900 t in the year 2001 (Sur *et al.*, 2003). Since 1985, MTBE is added in Germany to gasoline mainly as octane enhancer. Its concentrations of 0.43%, 3.0% and 10.2% (w/w) in regular, Euro super and super premium gasoline, respectively (Sur *et al.*, 2003), are nearly constant all year round. MTBE is highly water soluble (42 g/L at 20°C), adsorbs only weakly to soil ($\log K_{OC}$ = 1.05 at 20°C), has a low biodegradability and its taste and odor thresholds are in the range of 5-40 micrograms per liter (µg/L). These characteristics, together with its widespread use, have resulted in detectable concentrations in the aquatic environment in the USA and Europe (Squillace *et al.* 1996; MEF, 2001) and led to concern about the presence of MTBE in drinking water sources (Brauch *et al.*, 1999; Clawges *et al.*, 2001).

The risk for drinking water sources is mainly posed by point sources such as leaking pipelines or leaking underground storage tanks (LUSTs), since MTBE is able to travel far distances away from the point of release with the groundwater. Point sources are seen to lead to MTBE groundwater concentrations of more than 1-5 µg/L (Schmidt *et al.*, 2003) and past releases of MTBE may threaten drinking water sources in the U.S. over at least the current decade (Johnson *et al.*, 2000). Drinking water sources in Germany may also be affected by vicinal MTBE point source releases that remained undetected so far (Effenberger *et al.*, 2001).

In addition to groundwater, German rivers like the Rhine and Main represent a source for drinking water, since in Germany about 15-16% of the drinking water used is produced by bank filtration or artificial filtration (Achten *et al.*, 2002b). The analyses of water samples from these rivers revealed mean MTBE contents of about 0.2 µg/L and maximum concentrations of 2 - 10 µg/L (Sacher *et al.*, 2002; Achten *et al.*, 2002a). Riverbank filtration as the first step in the cleanup process of waterworks was shown not to eliminate MTBE completely. Thus, MTBE could be found in raw water of waterworks along these rivers and in finished drinking water produced by riverbank filtration and artificial infiltration (Sacher *et al.*, 2002; Achten *et al.*, 2002b). The concentrations of MTBE in raw water and finished drinking water were low and in the range of 35-180 ng/L. These concentrations are about one order of magnitude below the taste and odor thresholds of 5-40 µg/L. However, it is useful to determine the sources of MTBE in river water, since current cleanup technologies used in German waterworks are able to eliminate MTBE only with expensive modifications (Baus *et al.*, 2003).

MTBE can reach river water through a variety of sources. Rain and snow as diffusive atmospheric sources were shown to contain MTBE in the range of 10-85 ng/L (Achten *et al.*, 2001c) and 11-631 ng/L (Kolb and Püttmann, 2004, to be published), respectively. Results from Bender *et al.* (2000) suggest the atmosphere as source for MTBE in stream water in the U.S. even at median concentrations of 250 ng/L. This source should not be neglected, since emissions to air from the use of gasoline have been proposed to be the main source of MTBE releases to the environment (MEF, 2001). Another diffusive source is the introduction of MTBE into the receiving stream through (contaminated) groundwater. Further release scenarios include shipping of petrochemical products which can cause accidental releases mainly at loading/unloading facilities (MEF, 2001) and recreational boating (Reuter *et al.*, 1998; Dale *et al.*, 2000; An *et al.*, 2002). MTBE production/formulation sites located at rivers are also possible point sources of MTBE (MEF, 2001). MTBE input into surface water through groundwater contaminations, losses of MTBE during transport on waterways, recreational boating and releases at MTBE production/formulation sites yet may have been underestimated when modeling the MTBE distribution in the aquatic environment in Germany (Achten *et al.*, 2002c). Recently, the influence of MTBE contaminated groundwater and possible MTBE releases at production/formulation sites located at rivers was determined at three river sites in Germany (Kolb and Püttmann, 2004, to be published). However, there is still a lack of investigations in Germany regarding MTBE transport on waterways and the influence of recreational boating on MTBE concentrations in German surface water.

Sewage/industrial plant effluents were shown to be further sources of MTBE in river water (Brown *et al.*, 2001; Achten *et al.*, 2002a). In this context, industrial plants refer to production sites where MTBE is used as solvent or reagent. 1.5% of the MTBE produced in Europe in 1997 was used for reasons other than addition to gasoline (MEF, 2001). First investigations on MTBE in river water in Germany accompanied by investigations on the sources precipitation, industrial effluents and municipal sewage plant effluents were given by Achten *et al.* (2001c; 2002a). The results obtained so far suggest that industrial and sewage plant effluents might account for a major source of MTBE in rivers, whereas the influence of the MTBE input into surface water via precipitation is low based on results obtained from small rural creeks without major sewage water input (Achten *et al.*, 2002a). However, there has so far been a small amount of available data on MTBE in industrial and sewage plant effluents (n=82).

The objective of the present study was to further investigate the influence of these three sources on the basis of a generally enlarged sample amount, in particular an enlarged sample amount from industrial and sewage plants (n=217). The river used as study object was the lower part of the river Main. At the river Main, MTBE inputs via contaminated groundwater, via MTBE shipping, via recreational boating and via production/formulation sites could be reasonably omitted (see Chapter 8.4.2.). Thus, the river Main receives MTBE inputs mainly through precipitation and sewage water input. In a first step, long-term monitoring at the river Main was carried out at a representative location. The data obtained from this monitoring served as basis to compare the determined MTBE contents to concentrations obtained from samples taken at possible sources. The source precipitation was investigated by sampling precipitation about 3 km away from the monitoring point at the river Main over a period similar to the Main sampling. The MTBE concentrations in industrial plant effluents were obtained by analyzing effluent samples from different companies in the Rhine-Main area. Municipal sewage plant effluents were sampled at two sewage plants that were considered representative. Urban runoff and sewage plant influents were additionally sampled to provide information on the development of MTBE concentrations from precipitation to sewage water. In order to estimate the quantitative contribution of sewage plant effluents to the MTBE level in river water, the study conducted synchronized sampling of a sewage plant effluent and Main water upstream and downstream of the effluents' outfall.

8.3. Experimental

A rainwater collector on the top of a building 15 m above the ground in Frankfurt am Main (Frankfurt/M)-City (Georg-Voigt Strasse) was used for sampling precipitation from December 1998 to July 2003. The spot samples (n=89) were taken monthly, except during a period in winter 2000/2001 when samples were collected after every precipitation event. Detailed results of the precipitation samples and the ensuing urban runoff samples collected before 03/13/01 were discussed elsewhere (Achten *et al.*, 2001c).

The samples from the river Main (n=67) were collected from January 1999 to July 2003 by single-point grab sampling at a depth of about 30 cm below the surface of the water on the left river bank. These samples were collected monthly at the same location (Frankfurt/M-Friedensbrücke) at the Lower Main, about 3 km away from the precipitation sampling location and about 37 km from the mouth of the river Main into the river Rhine. On 04/28/03, 8 samples were collected within 8 hours at this location in order to investigate the short term variation of the MTBE concentrations at one sampling location. The results of the Main water samples collected before April 2001 were already published previously (Achten *et al.*, 2002a).

Industrial effluents (n=34) from 11 companies in the Rhine-Main area around Frankfurt/M were collected from June 2000 to April 2002. The sampling included different outfalls at each of the investigated industrial sites. The samples were collected over a period of 2 hours by the Hessisches Landesamt für Umwelt und Geologie (HLUG). The results of the industrial effluent samples collected before 2002 have been reported previously (Achten *et al.*, 2002a).

The effluents of the two municipal sewage plants Frankfurt/M-Niederrad (n=39) and Sindlingen (n=27), located in the Frankfurt/M area at the river Main, but downstream of the Main water monitoring point Frankfurt/M-Friedensbrücke, were sampled from November 2000 to July 2003. These sewage plants process the wastewater of 1,350,000 (Niederrad) and 470,000 (Sindlingen) people. The corresponding influents of the sewage plants, i.e. the influent "Griesheim" (n=39) and the influent "Niederrad" (n=39) of the sewage plant Niederrad, as well as the influent of the sewage plant Sindlingen (n=39) were also analyzed for their MTBE content. The samples were collected monthly, each over a period of 24 h, except the spot samples collected before 02/13/01. The resident time of the waste water in the sewage plants is 12-18 hours, so that the 24-hour sampling of influents and effluents could be considered representative. The results of the samples obtained before 03/09/01 were already summarized by Achten *et al.* (2002a).

In order to quantify the contribution of municipal sewage plants to MTBE contents in the river Main more detailed, spot sampling was performed during four different sampling events on 01/29/04, 02/16/04, 02/24/04 and 03/11/04. During these events, Main water was sampled in the middle of the river Main (Frankfurt/M-Griesheimer Brücke), about 1.5 km upstream of the outfall of the effluent of the sewage plant Niederrad. The outfall is located in the middle of the river. About 15 min later, spot samples were taken from the effluent of the sewage plant Niederrad and from the middle of the river Main, about 1 km downstream of the outfall

(Frankfurt/M-Schwanheimer Brücke). The concentrations measured were set in relation to the actual water flows of the Main and the sewage plant effluent.

The samples were collected in 100 ml sample vials (brown glass) with no headspace left and acidified with conc. HCl to pH 2. They were transported and stored at 4°C and analyzed within three weeks. During sampling and transport field blanks were always present and analyzed parallel to the samples. The analysis was performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS). Mass chromatography of m/z 73 (MTBE) and m/z 76 (internal standard d_3MTBE) was used for quantitation. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. The detection limit was 10 ng/L with a relative standard deviation of 11%. A detailed description of the analytical method is published elsewhere (Achten *et al.*, 2001b), with the exception of the use of a J&W Scientific DB-624 column (60 m x 0,32 mm) with a film thickness of 1.8 µm for compound separation in the GC.

8.4. Results and Discussion

8.4.1. Precipitation Frankfurt/M-City

89 precipitation samples were collected. MTBE was detectable in 60% of the samples at concentrations ranging from 11-92 ng/L. The median (mean) concentration was 30 ng/L (36 ng/L). Overall, MTBE was less or non-detectable in precipitation in the months from April to September (Figure 8-1). Except of three samples taken on 08/18/99, 06/17/01 and 08/20/02 respectively, MTBE was non-detectable in precipitation from May to August. The median (mean) MTBE concentration calculated without samples below the detection limit was 30 ng/L (36 ng/L). The maximum concentrations of 92 ng/L and 85 ng/L occurred on 12/15/02 and 11/01/00, respectively. In winter 2000/2001, when every precipitation event was sampled, the detection of MTBE was dependent on ambient temperatures. In precipitation collected at temperatures below 15°C (average daily temperatures) and in the first precipitation after a dry period the concentration of MTBE was higher than in precipitation collected during or at the end of a wet period (washout-effect) (Achten *et al.*, 2001c).

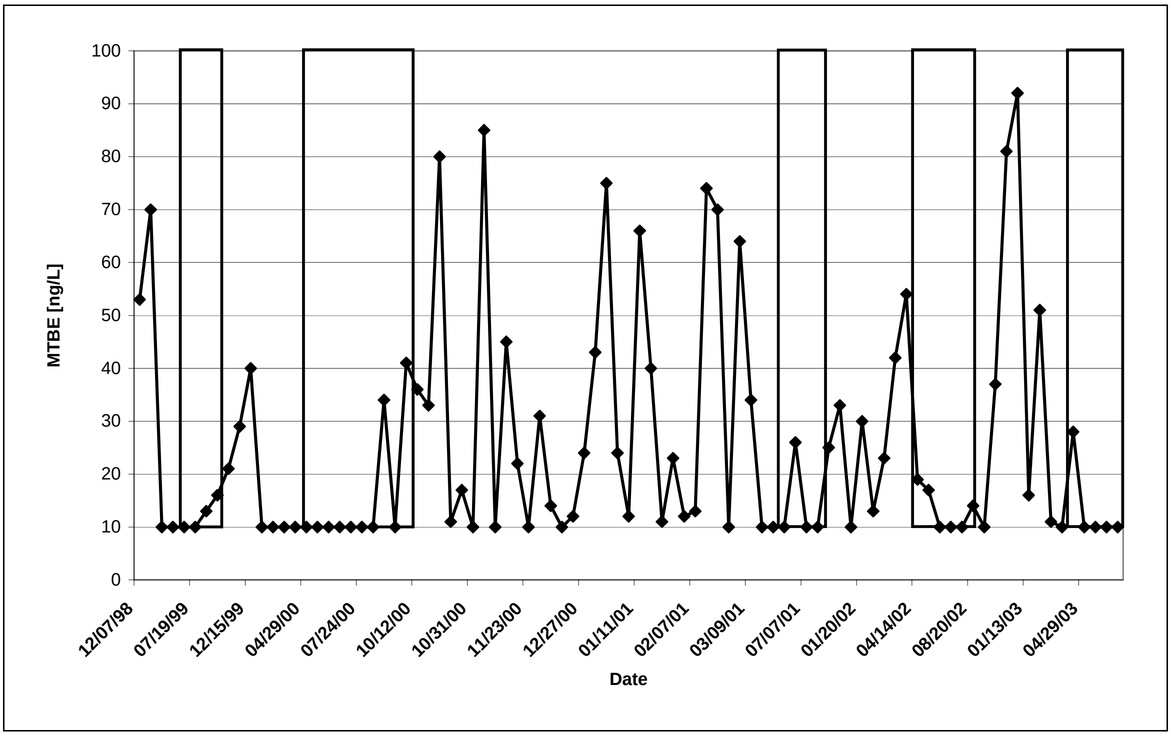

Figure 8-1: MTBE concentrations in precipitation samples collected from 12/07/98-07/24/03 at Frankfurt/M-city. The detection limit was 10 ng/L with a relative standard deviation of 11%. The marked time periods refer to the months April-September. Data from 12/07/98-03/12/01 were published by Achten et al., 2001c. For single results see Appendix Table A11.

The lower amounts of MTBE in precipitation in warmer months is mainly due to the higher photochemical activity and in addition to the increased Henry's law coefficient of MTBE at increased temperatures (Fischer *et al.*, 2004). The urban air as potential MTBE source was previously identified by seasonally dependent detection frequencies in stormwater in the U.S. (Lopes and Bender, 1998), since the MTBE amounts in gasoline in different regions in the U.S. are seasonally dependent. In contrast, the seasonal pattern that could be observed during the monitoring in Frankfurt/M is due rather to ambient meteorological conditions, because the MTBE concentrations in German gasoline are almost constant all year round.

8.4.2. Main Frankfurt/M-Friedensbrücke

From January 1999 to July 2003, MTBE concentrations in the river Main at the monitoring point Frankfurt/M-Friedensbrücke were in the range of 13-985 ng/L (06/26/03) (Figure 8-2). MTBE was not detectable in two samples from 12/08/99 and 01/14/99. The median (mean) concentration was 66 ng/L (125 ng/L).

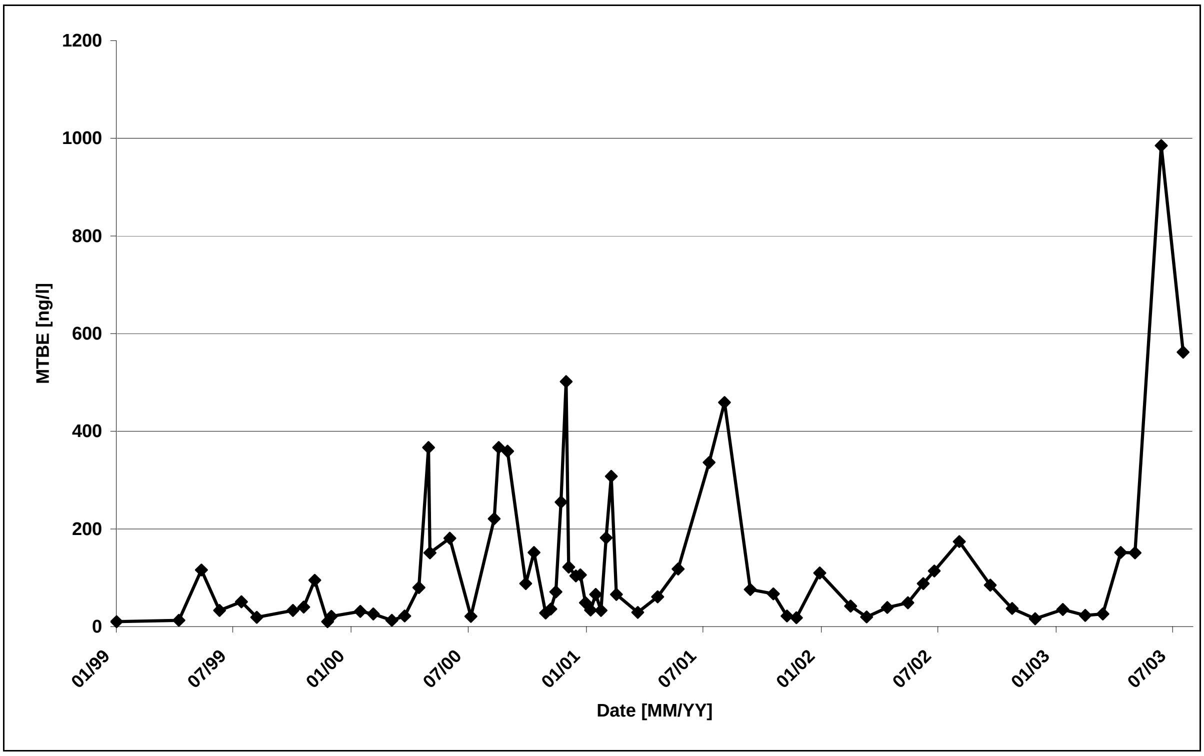

Figure 8-2: MTBE concentrations in Main water samples collected from 01/14/99-07/30/03 at the monitoring point Frankfurt/M-Friedensbrücke. The detection limit was 10 ng/L with a relative standard deviation of 11%. Data from 01/14/99-03/01/01 were published by Achten et al., 2002a. For single results see Appendix Table A9.

The concentrations that were found in the river Main are comparable to results of other studies investigating MTBE in German river water (Sacher *et al.*, 2002; Püttmann *et al.*, 2002). They are also comparable to U.S. data, since MTBE concentrations in creeks and streams in the U.S. were reported in the range of 150-1600 ng/L with median values of about 300 ng/L to 420 ng/L (Bender *et al.*, 2000; Reiser and O'Brien, 1998). If a water flow in the Main of 190 m^3/s is estimated as average, the calculated median concentration corresponds to a theoretical loading of about 0.4 t/a between January 1999 and July 2003. The different concentrations measured in the years of observation can be divided into three parts. From January 1999 to April 2000, the median MTBE concentration was 29 ng/L, followed by a period from May 2000 to August 2001 with a median concentration of 118 ng/L. From August 2001 to May 2003, the median concentration again was lower with 46 ng/L, followed by the maximum concentrations of 985 ng/L and 562 ng/L in June 2003 and July 2003, respectively. The reason for the observed variations within these 4.5 years remained unclear. The MTBE concentrations in the Main might have been influenced by different hydrological and meteorological conditions. A fit of the concentrations measured from 1999-2000 with the water stages of the river in the same period (Wiechmann, 2004) did not reveal a good correlation (n=30, R^2=0.12; data not shown). The 8 samples taken on 04/24/03 were an approach to investigate the influence of the ambient water temperature and to obtain data on the variations of the concentrations during one day. The samples showed MTBE concentrations between 96 ng/L and 234 ng/L (Figure 8-3) with a mean concentration of 130 ng/L. The ambient water temperature increased only from 13°C to 14.5°C and there was apparently no visible influence of temperature on the measured MTBE concentrations. The daytime variation of MTBE concentrations may lead to the conclusion that unknown point sources release highly variable amounts of MTBE into the river. This is confirmed by the high fluctuation of MTBE concentrations obtained during the 4.5 years of Main water sampling. In order to identify the sources, the Main data were compared to the data from possible sources.

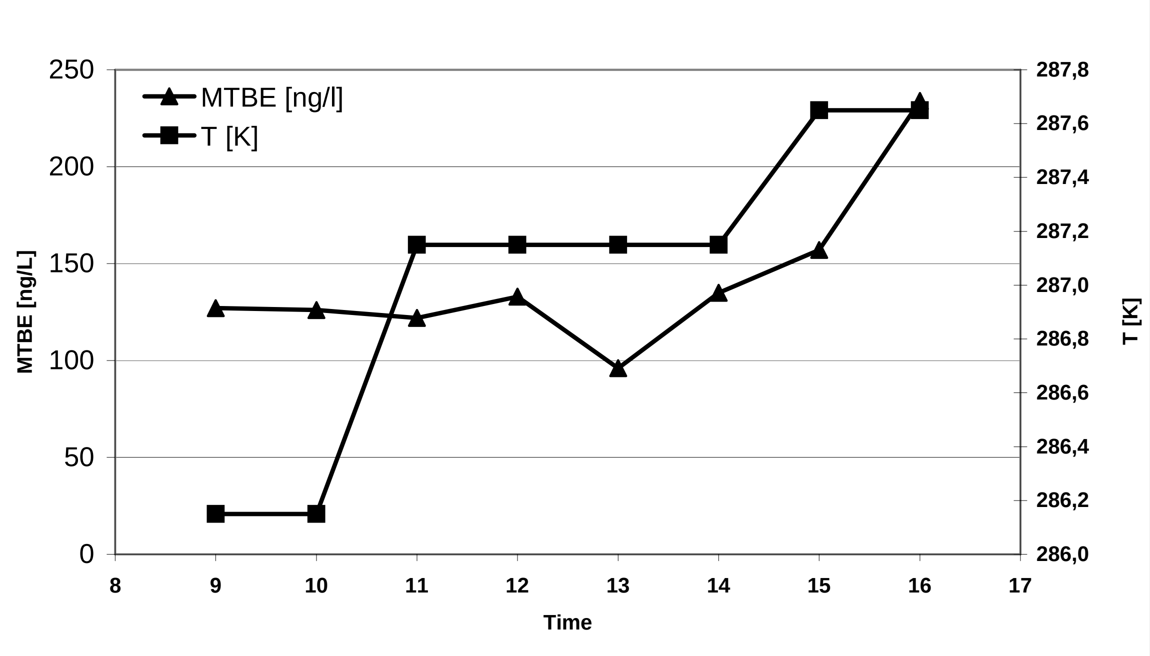

Figure 8-3: MTBE concentrations and ambient water temperature in the river Main at Frankfurt/M-Friedensbrücke on 04/24/03. The detection limit was 10 ng/L with a relative standard deviation of 11%. For single results see Appendix Table A9.

The atmospheric MTBE input via precipitation is in the range of about 30 ng/L as suggested by concentrations measured in small rural creeks (Achten *et al.*, 2002a). A similar contribution of this MTBE source in the river Main would also lead to concentrations not exceeding 30 ng/L.

Compared to the median (mean) concentration measured in precipitation in Frankfurt/M-City, the value in the river Main is more than two (three) times higher. In addition, a seasonal dependency of the MTBE amounts in the river Main could not be observed. Therefore, a background concentration in the river Main at Frankfurt of about 30 ng/L, equivalent to the median MTBE concentration measured in precipitation in Frankfurt/M, might be attributed to the direct input via precipitation. However, even the concentration of 30 ng/L most probably represents maximum contributions, since the precipitation data are based on monitoring results from the metropolitan area of Franfurt/M. The river Main mainly contains rural precipitation with very low MTBE concentrations that reaches the river Main via many rural creeks.

Other MTBE sources such as the input via contaminated groundwater could not be investigated, as well as MTBE releases from MTBE shipping and recreational boating activities. To our knowledge, at the lower river Main, where the monitoring point is located, no large groundwater contaminations dewater into the Main. The MTBE emissions to surface water during transportation of MTBE and at loading/unloading harbor facilities are difficult to calculate and they were considered to be out of the scope of the EU risk assessment on MTBE (MEF, 2001). In the year 2003, the freight traffic on the Main was 17,081,275 t and of this amount, 4,208,067 t (ELWIS, 2003) were oil and petrol related products. However, no MTBE production/formulation sites with possibly leaking loading/unloading facilities are located upstream of the monitoring point at the river Main (Pahlke *et al.*, 2000; MWV, 2004). Varying MTBE concentrations in the river Main were probably also the result of diffusive and intermittent MTBE input caused by recreational boating activities. Concentrations ranging from <0.1 µg/L to 29 µg/L were found in the U.S. in lakes used for recreational boating (Reuter *et al.*, 1998; Dale *et al.*, 2000; An *et al.*, 2002) and in a recreational harbor (Zuccarello *et al.*, 2003). In Dutch surface water, where recreational boating is very popular, MTBE concentrations of 1.5 µg/L to 7.0 µg/L could be found (Miermanns *et al.*, 2000) and the analyses of two spot samples taken during the present study in the Vecht at Maarsen (NL) (07/25/02) and in a marina at Gouda (NL) (07/21/02) (Table A10 in the Appendix) revealed MTBE concentrations of 1.0 µg/L and 1.1µg/L. The recreational boating activities on the river Main during the long-term monitoring were observed to be low and should not have contributed significantly to the MTBE content in the river water. Because contaminated groundwater, losses of MTBE during transport, recreational boating and MTBE production/formulation sites could be reasonably ruled out as possible sources, the measured MTBE concentrations at the monitoring point Frankfurt/M-Friedensbrücke could most probably assigned mainly to inputs from precipitation and sewage water. Thus, these concentrations could be compared to the MTBE concentrations obtained by analyzing samples from industrial sewage plants, which do not represent MTBE production/formulation sites and to MTBE concentrations in municipal sewage plant effluents.

Industrial effluents and an overall of approximately 97 municipal sewage plants (Land Bayern, 2004; HLUG, 2004) are located directly at the river Main. Among the 97 sewage plants, there are seven municipal sewage plants upstream of the monitoring point, each processing wastewater of more than 100,000 people similar to the sewage plants Sindlingen and Niederrad. Therefore, the investigated industrial and sewage plant effluents were considered as representative and might provide an appropriate contribution to the understanding of these release scenarios.

8.4.3. Industrial Plant Effluents

From June 2000 to April 2002, industrial effluent samples of 11 companies located in the Rhine-Main area were collected (Figure 8-4). Four of the industrial effluents are located at the river Rhine; seven of them dewater into the river Main. Two of the seven outfalls dewatering into the river Main are located upstream of Frankfurt/M-Friedensbrücke, the monitoring point at the river Main. The median (mean) MTBE concentration calculated from all industrial effluent data was 156 ng/L (2214 ng/L). Exceptional high concentrations of 12 µg/L, 28 µg/L and 7µg/L were measured in the effluents of companies 2, 4 and 8, which are not located upstream of Frankfurt/M-Friedensbrücke. The releases at the effluents of the companies 2, 4 and 8 were most probably due to the use of MTBE as solvent or as reagent, but might also originate from gasoline used for logistic reasons. The concentrations determined in the remaining industrial effluent samples generally were low with a median (mean) MTBE concentration of 49 ng/L (329 ng/L). These concentrations are similar to those previously found in river water in Germany and in the range of the Main water concentrations. Therefore these effluents contribute to increased background concentrations, i.d. concentrations higher than background concentrations caused by the direct atmospheric input. The varying MTBE concentrations in the same outfalls of the effluents of companies 2, 4 and 8 (Figure 8-4) indicate that industrial discharge of MTBE into river water is discontinuous. The concentrations in these effluents are one order of magnitude higher than the concentrations measured at the monitoring point at the river Main. These effluents can be seen as discontinuous point sources (Achten *et al.*, 2002a).

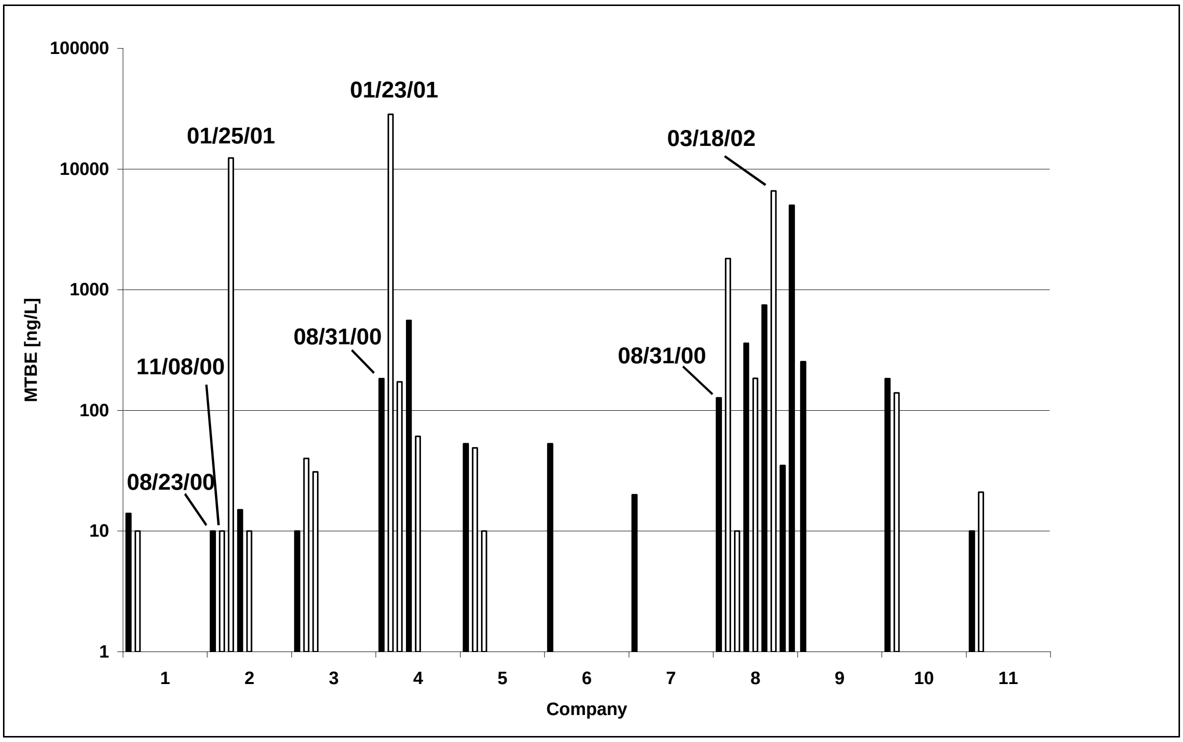

Figure 8-4: MTBE concentrations in water samples (n=34) from effluents of different industrial plants in the Rhine-Main area from 06/13/00-04/29/02. In the areas of companies 2, 4 and 8, different outfalls were sampled. The columns marked with dates represent the same outfall tubes sampled at different dates. The detection limit was10 ng/L with a relative standard deviation of 11%. Data from 19 samples originate from Achten et al., 2002a. For single results see Appendix Table A13.

Although these releases are diluted in the river water system, plumes may occur, leading to MTBE "waves", i.e. enhanced MTBE concentrations far away from the release point (Sacher *et al.*, 2002). In contrast to more continuous releases like groundwater contaminations, e.g. detected at the river Saale at Leuna (Kolb and Püttmann 2004, to be published), these waves are only temporally observable, due to their discontinuous release. Elevated MTBE concentrations ranging from 500 ng/L to 25 µg/L in the Lower Rhine were detected by continuously monitoring automatic systems indicating intermittent MTBE releases from yet unknown sources (Gehrke *et al.*, 2003). The maximum MTBE concentrations of about 0.4-1 µg/L measured in the river Main during the monitoring might represent such waves possibly originating from sources far away from the monitoring point.

8.4.4. Municipal Sewage Plant Effluents

The results of the analyses of samples from the effluents and influents of the sewage plants Niederrad and Sindlingen are shown in Figure 8-5. Concentrations higher than 1 µg/L could only be observed in the influent of the sewage plant Niederrad (154,000 m^3/d) and the effluent of the sewage plant Niederrad, where the maximum concentration of 3162 ng/L was measured on 01/11/02. The influent of Niederrad contains primarily industrial sewage water, whereas the influent "Griesheim" (213,000 m^3/d) and the influent of the sewage plant Sindlingen (75,000 m^3/d) mostly represent domestic sewage water. These origins were reflected by the median (mean) concentrations calculated: The highest values were obtained for the influent "Niederrad" with 256 ng/L (438 ng/L). The median (mean) concentrations of 112 ng/L (187 ng/L) and 87 ng/L (124 ng/L), calculated for the influents "Griesheim" and "Sindlingen", were lower. Urban runoff is also transported to the sewage plants, since the sewage system of Frankfurt/M is a mixed system, where the runoff is mixed with the domestic/industrial wastewater and is then processed in the sewage plants.

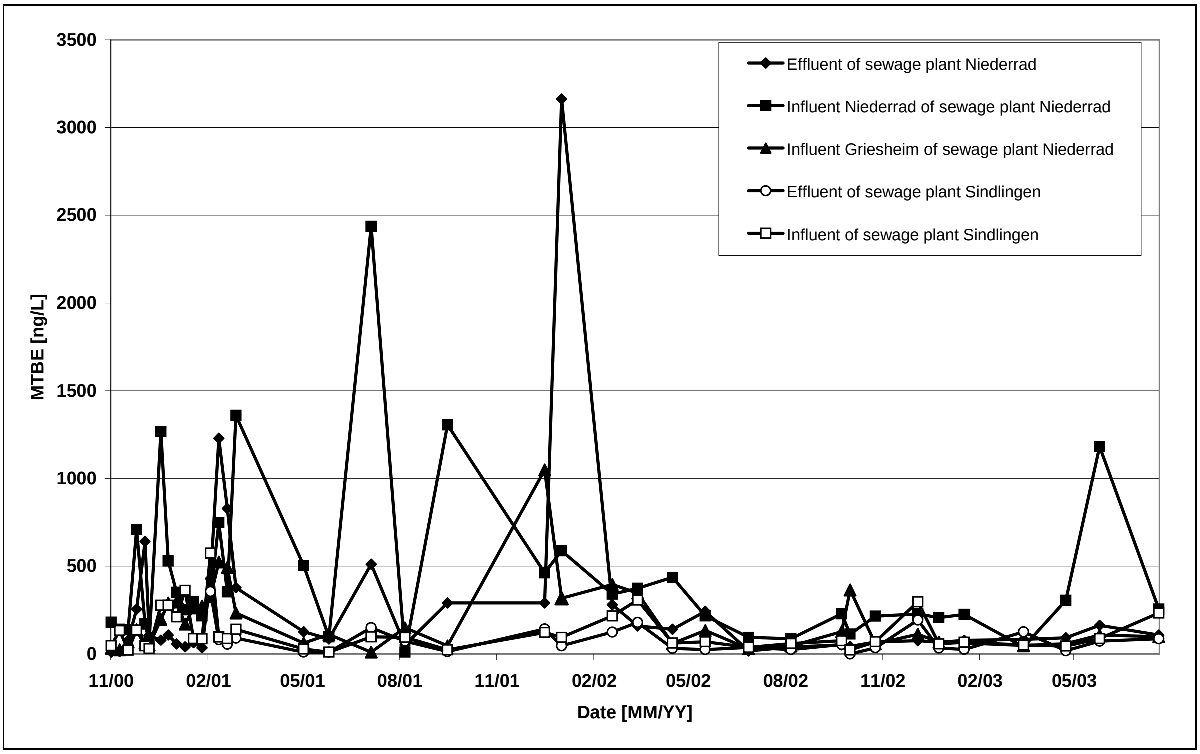

Figure 8-5: MTBE concentrations in effluents and influents of sewage plants in the Frankfurt/M area from 11/11/00-07/30/03. The detection limit was10 ng/L with a relative standard deviation of 11%. Data from 11/11/00-03/01/01 were published by Achten et al., 2002a. For single results see Appendix Table A12.

Only in the case of heavy rainfall, the urban runoff is partly discharged directly into the river Main. In addition to the precipitation samples in Frankfurt/M, ensuing urban runoff samples were analyzed. 12 samples of urban runoff were taken 500 m away from the precipitation sampling in a ditch close to a high traffic road. These samples provided a wide concentration range of MTBE from 30 ng/L to 1174 ng/L with a mean concentration of 204 ng/l. On the basis of the restricted sample number only rough estimations could be made. When comparing the urban runoff to the corresponding precipitation samples, the results indicated that about 20 % of the MTBE in urban runoff may have been transported in the atmosphere before its uptake by precipitation (Achten *et al.*, 2001c). Results from studies conducted by Lopes and Bender (1998) and Borden *et al.* (2002) have shown that MTBE in stormwater is associated with urban land surfaces (Lopes and Bender, 1998), that the average proportion of impervious surface possibly correlates with MTBE concentrations (Lopes and Bender, 1998) and that higher MTBE concentrations could be associated with runoff from gas stations (Borden *et al.*, 2002). Although urban air potentially is an important source of MTBE in urban waters (Lopes and Bender, 1998), the investigations on urban runoff and stormwater suggest a direct uptake of MTBE at roads and gas stations leading to increased MTBE amounts in the urban runoff, compared to precipitation. However, the percentages originating from urban runoff of the MTBE contents that were found in the influents of the sewage plants could not be determined due to mixing with domestic/industrial wastewater. A low proportion of the MTBE present in the influents of the sewage plants could be attributed to MTBE, that is already present in drinking water in Frankfurt/M at a median concentration of 37 ng/L (Kolb and Püttmann 2004, to be published).

According to the data obtained from the sewage plants Niederrad and Sindlingen, about 50% (Niederrad) and 38% (Sindlingen) of the MTBE is eliminated through the wastewater processing and loadings of about 9-14 kg/a (Niederrad) and 2 kg/a (Sindlingen) are calculated. These loadings are slightly lower than the loadings calculated by Achten *et al.* (2002a) of 10-37 kg/a (Niederrad) and 2-5 kg/a (Sindlingen). The elimination rates are slightly higher than the rates determined previously at 33% for Niederrad and 31% for Sindlingen (Achten *et al.*, 2002a).

The median (mean) concentration of the effluent of the sewage plant Niederrad was higher with 92 ng/L (271 ng/L) than the median (mean) concentration of 55 ng/L (81 ng/L) calculated for the effluent Sindlingen. Especially the maximum concentration of 3162 ng/L measured in the effluent Niederrad indicates that, similar to the industrial effluents, the MTBE releases via sewage plants can be seen as point sources of MTBE into river water. However, exceptional high MTBE amounts of up to 28 µg/L found in industrial effluents could not be measured in sewage plant effluents. Considering that about 97 municipal sewage plants are located directly at the river Main and considering the data obtained from the two sewage plants, the input of MTBE from these sources contributes to the increased background concentrations of MTBE in the course of the river Main. The median and mean concentrations of the effluents are in the range of median and mean Main water MTBE concentrations and the input occurs more continuously than via industrial effluents. About 89 of the 97 municipal sewage plants at the river Main are located upstream of the monitoring point at Frankfurt/M-Friedensbrücke, including the seven sewage plants with comparable capacities to Niederrad and Sindlingen. Effluents of publicly owned treatment works (POTWs) treating municipal wastewater were also investigated in Southern California/USA (Brown *et al.*, 2001) and concentrations in the range of <5-123.3 µg/L were determined. The POTWs accounted for the greatest proportion of the daily mass emission of MTBE, although the effluents of refineries contained the highest concentrations. However, it should be noted that the high mass emissions of up to 164 kg/d calculated in the Southern California study could be attributed not only to the inputs via domestic wastewater and urban runoff, but also to discharges from refinery wastewater (Brown *et al.*, 2001). This source is not present in the catchment area of the two sewage plants investigated in the present study.

8.4.5. Sampling in Vicinity to the Outfall of the Sewage Plant Niederrad

Although the results from the investigation on the effluents of municipal sewage plants indicated these outfalls as punctual MTBE sources in river water, little is known about the proportion that one effluent contributes to the overall MTBE amounts in the receiving stream. Therefore, synchronized sampling at the effluent Niederrad and the Main before and after the outfall of the effluent was conducted. The results and the calculations carried out by use of additional information on the water flows of the Main and the effluent are summarized in Table 8-1. The MTBE amounts that were found in the effluent samples generally were higher than those in the Main water. Except the outlier on 03/11/04, the concentrations in the Main water downstream of the outfall were higher than in the Main water samples upstream of the outfall. The highest increase of 57.14% was observed on 01/29/04. During this sampling event, the water flow of the effluent was 2.29% of the Main water flow. On the other days, the contribution of the effluent water was lower and in the range of 0.82% to 0.95%. Except at the sampling on 03/11/04, the theoretical increase of the MTBE contents in the Main water downstream of the outfall generally was lower by a factor of 6-49 than the measured increase. The highest theoretical increase (8.64%) was calculated for the samples collected on 01/29/04, when also the highest increase was observed (57.14%). The discrepancy between the calculated and the measured increases might be due to the fact that the samples from the river Main were taken only 1 km away from

Date	**01/29/04**	**02/16/04**	**02/24/04**	**03/11/04**	**Ø**
MTBE concentration in Main water upstream of the outfall [ng/L]	49	167	184	81	120
MTBE concentration in Main water downstream of the outfall [ng/L]	77	190	215	69	138
Increase [%]	57,14	13,77	16,85	-14,81	18,24
MTBE concentration effluent [ng/L]	238	312	264	296	278
Main water flow [m^3/s]	131	231	154	116	158
Water flow effluent [m^3/s]	3	1,9	1,4	1,1	1,85
% of Main water flow	2,29	0,82	0,91	0,95	1,24
calculations: Theoretical MTBE concentration in Main water downstream of the outfall [ng/L]	53	168	185	83	122
Theoretical increase [%]	8,64	0,71	0,39	2,49	1,51

Table 8-1: Results of the synchronized samplings at the effluent of the sewage plant Niederrad and upstream and downstream of the outfall of the effluent at the river Main.

the sewage plant outfall. Because the sampling point and the outfall were both located in the middle of the river, the downstream sample may represent the plume that was formed downstream of the outfall. In this case, the downstream samples would not have been representative for the Main water at this point.

However, the results indicate a theoretical contribution of the sewage plant effluent water to the MTBE contents in the Main of up to 9%. This proportion may be even higher when the water stage in the river is low and/or when heavy precipitation occurs and the influent capacity of the sewage plant Niederrad of 6.7 m^3/s is exceeded. In this case, a significantly higher amount of water including urban runoff can reach the Main via overfall basins. This additional water may contain higher MTBE concentrations since the overfall water in this case has not gone through the complete sewage process. Given the exceptionally high concentrations measured in industrial effluents, even higher (discontinuous) inputs from these sources can be estimated. These inputs may be reflected in the maximum MTBE concentrations in the Main that were detected in the long-term monitoring.

8.5. Conclusions

The long-term MTBE monitoring of Main water and precipitation in Frankfurt/M from 1999 to 2003 revealed no significant changes of the MTBE contents compared to previous results that covered data from 1999 to 2001 (Achten *et al.*, 2001c; Achten *et al.*, 2002a). MTBE could be detected in 60% of the precipitation samples at a median (mean) concentration of 30 ng/L (36 ng/L). MTBE generally was more detectable in the months from October-March. The median (mean) MTBE concentration in the river Main was determined at 66 ng/L (125 ng/L). By comparing the median values in precipitation and the river Main it can be concluded that only background concentrations of MTBE in river water of about 30 ng/L may be attributed to the direct atmospheric input via precipitation. Because the precipitation data are based on monitoring results from the metropolitan area of Frankfurt/M, the concentration of 30 ng/L most probably represents a maximum contribution. The results of the investigations on industrial and sewage plant effluents indicate that the largest and second largest sources of MTBE in river Main water are industrial and sewage plant effluents including urban runoff, respectively. This confirms previous findings of Achten *et al.* (2002a) and is based on a larger data set. Three industrial effluents were shown to contain MTBE up to 28 μg/L. The varying concentrations in these outfalls point to them as discontinuous point sources causing intermittent MTBE “waves” in rivers that may be detected as maximum concentrations during long-term monitoring. The remaining industrial effluents and the effluents of two municipal sewage plants showed median (mean) MTBE concentrations of 49 ng/L (329 ng/L), 92 ng/L (271 ng/L) (Niederrad) and 55 ng/L (81 ng/L) (Sindlingen). These concentrations are in the range of Main water MTBE concentrations and it can be concluded that these effluents contribute to increased background concentrations of MTBE in rivers such as the Main. Elimination rates of 50% and 38% were calculated for the sewage plants Niederrad and Sindlingen, respectively. The theoretical loadings were determined at 9-14 kg/a (Niederrad) and 2 kg/a (Sindlingen).

The detailed sampling of Main water upstream and downstream of the outfall of the sewage plant Niederrad revealed quantitative results regarding the contribution of sewage plant effluents to the

MTBE amounts in the river Main. A contribution of up to 9% could be calculated, but this contribution may increase in the cases of heavy precipitation events and industrial effluents. The shipping of petrochemical products including MTBE and recreational boating as MTBE sources in river water still remain to be investigated.

9. CONCLUSIONS AND FUTURE IMPLICATIONS

The present study and the results of the interlaboratory study (Schumacher *et al.*, 2003) confirmed the findings of Achten *et al.* (2001b), that HS-SPME combined with GC/MS is a suitable method to analyze MTBE in environmental water samples with the necessary accuracy and precision in the ng/L–range. The application of the method was focused on the analysis of samples collected to get answers to the questions created by the results obtained by Achten (2002) previously.

MTBE is present in finished drinking water from certain drinking water systems in Germany. Although the concentrations found were mainly below 100 ng/L and thereby far below toxicological or taste and odor thresholds, these findings may not be considered tolerable, since MTBE is an anthropogenic substance. Therefore, MTBE is relevant for drinking water production, at least at locations, where raw water for the production of drinking water is influenced by riverbank filtered water (e.g. at the river Rhine) or groundwater possibly affected by contaminations (e.g. at the Leuna site). Similar important as the development of technologies to eliminate MTBE from raw water is the investigation on MTBE releases into drinking water resources, given the findings obtained from bank filtered water. The present study showed that sites, where large amounts of MTBE are produced, stored or used for formulation can be release sources not only through process wastewater, but also through contaminated groundwater dewatering into the receiving stream. The results obtained at the investigated production/formulation/storage sites with MTBE concentrations in the corresponding river water of up to 5 µg/L will at least in part explain the underestimation of direct MTBE releases into river water in Germany that led to the lower model predictions of MTBE concentrations in German surface water compared to monitoring data (Achten *et al.*, 2002c). The sewage water from industrial plants, where MTBE is used as solvent or reagent and municipal sewage plant effluents (associated to urban runoff) were previously identified as further release sources of MTBE into river water. The present study confirmed these findings on the basis of a larger data set. The median concentrations that were found in these effluents were up to 100 ng/L and maximum concentrations in industrial effluents up to 28 µg/L could be observed. The discontinuous industrial input of large MTBE amounts can lead to MTBE “waves” in the rivers. An average contribution of 9% by a single municipal sewage plant effluent to the MTBE contents in river water was determined. The investigation of industrial/municipal sewage plant effluents also required a long-term monitoring of the MTBE contents in water from the river

Main and precipitation, where no increasing MTBE concentrations during the last five years could be observed. The direct atmospheric input of MTBE via precipitation was confirmed to be visible only in small rivers without sewage water input. The median concentrations found in precipitation and the river Main were 30 ng/L and 66 ng/L, respectively. In contrast to rainwater, snow was shown in the present study to contain MTBE at similar concentrations in samples from urban and rural locations. Although the maximum concentrations found often were higher than 100 ng/L compared to rainwater, the MTBE input via snow was not considered to be a significant risk for drinking water resources. Further findings of the investigation of snow samples were, similar to rainwater, a temperature dependence and the occurrence of wash-out effects. The MTBE input via precipitation or snow may also have been accounted for some of the MTBE detections in urban and non-urban shallow groundwater. MTBE was more detectable in urban than in non-urban groundwater samples. The uptake of MTBE through small point sources, i.e. gasoline spills at motorways, at gas stations or releases at industrial sites and the superimposition of remote point sources and diffusive (atmospheric) input creates difficulties to unequivocally assign the occurrence of MTBE to the mentioned sources. From the detections of MTBE at concentrations up to the mg/L-range in groundwater at gasoline contaminated sites and at one industrially influenced site investigated in the present study the question arises, how much sites in Germany exist, where MTBE still remained undetected. Finally, the MTBE findings in groundwater (up to 2 µg/L) from water protection areas led again to the conclusion, that MTBE is relevant for the production of drinking water.

The widespread occurrence of an organic substance about 18 years after its introduction in Germany is not desireable, at least due to precautionary aspects. The presence of MTBE even in finished drinking water or in precipitation expectedly results, when a persistent organic compound is used in large amounts in a bulk product like gasoline. The fact that after the usage of leaded organic compounds and aromatics the following compound MTBE again caused serious environmental problems has to be kept in mind when decisions are made of how to deal with this problem in the next years. A too fast solution, i.e. the immediate phase-out of MTBE in Europe by its substitution with another compound should be avoided, if the “lessons” (Chang and Last, 1998) from the MTBE story have been learned. Before substitutes are introduced, the MTBE problem continues to exist and known and still undetected serious groundwater contaminations may threaten drinking water sources over the next years. Therefore, it is important to develop and further economically improve remediation technologies for a substance that, similar to the chlorinated hydrocarbons, was considered first to be not remediable. Furthermore, the existing measures of protection recommended by the EU must be implemented in the national laws of the member states. In future monitoring programs toxic degradation products like TBA should be considered. Models are a useful tool to get an overview of the potential threat a substance may cause to the environment. However, it is the opinion of the writer, that future predictions of more than 1-2 years on problems of this kind that were obtained only by modeling, imply too much uncertainties and should not be used as basis by decision makers. Authorities responsible for new and growing gasoline markets like Eastern Europe and especially Asia should be in time aware of the MTBE problem. The emission controls are important on the background of the requirements of the EU directive 98/70/EG, but they may only serve as prevention as long as the "intermediate step" (Sur *et al.*, 2003) of using a persistent chemical like MTBE in gasoline is completed. Before a "new" substance is introduced in such substantial amounts like MTBE, its potential environmental, toxicological and economical impacts should be sufficiently evaluated and in particular all compartments of the environment should be considered. This means that future decisions focused on environmental questions recommend more "interconnected thinking" (Vester, 2000). The introduction of alternative engine technologies like fuel cells may avoid future problems not only related to MTBE, but also generally related to the use of fossile fuels.

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KEYWORDS

English

MTBE, Oxygenate, SPME, VOC, GC/MS, Drinking Water, Community Water System, River Water, Lippe, Wesel-Datten-Kanal, Saale, Rhine, Main, Precipitation, Rain, Snow, Groundwater, Wastewater, Sewage Plant, Effluents

German

MTBE, Oxygenat, SPME, GC/MS, Trinkwasser, Trinkwassernetz, Flüsse, Lippe, Wesel-Datten-Kanal, Saale, Rhein, Main, Niederschlag, Regen, Schnee, Grundwasser, Abwasser, Kläranlage, Einleitungen

ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CAAAs	Clean Air Act Amendments
d_3MTBE	deuterated Methyl Tertiary-Butyl Ether
DAI	Direct Aqueous Injection
DIPE	Di-Isopropyl Ether
ETBE	Ethyl Tertiary-Butyl Ether
EQC	Equilibrium Criterion
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HS	Headspace
HC	Hydrocarbon
$LogK_{OW}$	Logarithmic Octanol/Water Coefficient
$LogK_{OC}$	Logarithmic Water/Organic Carbon Coefficient
LUST	Leaking Underground Storage Tank
MAK	Maximale Arbeitsplatzkonzentration
MON	Motor Octane Number
MS	Mass Spectrometry
MTBE	Methyl Tertiary-Butyl Ether
Next-TAME	C_4-C_7 Tertiary Alkyl Methyl Ethers
NMR	Nuclear Magnetic Resonance
n.a.	not available
n.i.	no information
n.d.	not detected
NAWQA	National Water Quality Assessment Program
Oxyfuel	Oxygenated Fuel
P&T	Purge and Trap
PAH	Polycyclic Aromatic Hydrocarbon
PCE	Perchloroethene (Tetrachloroethene)
PDMS	Polydimethylsiloxane
PID	Photoionization Detector

RFG	Reformulated Gasoline
RON	Research Octane Number
RSD	Relative Standard Deviation
SIM	Single Ion Monitoring
SPME	Solid Phase Microextraction
TAME	Tertiary-Amyl Methyl Ether
TBA	Tertiary-Butyl Alcohol
TBF	Tertiary Butyl Formate
TCE	Trichloroethene
VOC	Volatile Organic Compound

APPENDIX

Measured MTBE Concentrations (ng/L)

Table A1: Finished Drinking Water

Location	Sampling Date	MTBE [ng/l]
Frankfurt/M-City	11/16/00	54
Frankfurt/M-City	11/25/00	<10
Frankfurt/M-City	12/14/00	20
Frankfurt/M-City	12/21/00	17
Frankfurt/M-City	12/27/00	18
Frankfurt/M-City	01/04/01	42
Frankfurt/M-City	01/12/01	25
Frankfurt/M-City	01/19/01	71
Frankfurt/M-City	01/28/01	42
Frankfurt/M-City	02/03/01	63
Frankfurt/M-City	02/14/01	32
Frankfurt/M-City	02/22/01	33
Frankfurt/M-City	03/01/01	29
Frankfurt/M-City	06/04/02	96
Frankfurt/M-Sossenheim	06/04/02	37
Frankfurt/M-Nordend	06/06/02	38
Aachen	06/09/02	<10
Aachen	06/09/02	<10
Muenster	06/14/02	<10
Leipzig Suedost	08/20/02	<10
Leipzig Zentrum	08/20/02	<10
Berlin Hosemannstr.	08/24/02	17
Berlin Cyanenstr.	08/24/02	<10
Freiburg	10/31/02	<10
Stuttgart	06/27/02	<10
Muenchen Airport	07/01/02	<10
Muenchen Tumblingerstr.	07/01/02	<10
Saarbruecken	07/08/02	<10
Darmstadt	06/20/02	<10
Solingen	06/16/02	<10
Dresden	07/25/02	<10
Dortmund	08/07/02	<10
Hamburg-Eimsbuettel	05/23/03	<10
Hamburg-Mitte	05/23/03	<10
Endingen	06/03/02	<10
Vreden	06/16/02	<10
Homberg/O Whg	08/15/02	<10
Homberg/O Garten	08/15/02	<10
Dorsten	05/08/03	<10
Haltern	05/08/03	<10
Marl	05/08/03	<10
Marl-Huels	05/08/03	<10
Wiesbaden-Biebrich	06/07/02	34
Koeln	06/23/01	56
Koeln 2	06/23/01	53
Duesseldorf	10/12/02	25
Duesseldorf Altstadt	10/27/02	48
Duesseldorf	05/07/03	38
Duisburg	05/07/03	15
Duisburg-Beekerwerth	05/07/03	<10
Basel	05/24/03	17
Kehl	10/18/02	<10
Ettlingen	05/27/03	<10
Karlsruhe Moebel	06/10/02	12
Karlsruhe	10/18/02	31
Karlsruhe Sued	05/27/03	<10
Karlsruhe Moebel	05/27/03	<10
Mannheim	05/27/03	<10
Mannheim McD	06/10/02	<10
Mannheim Baerb.	10/25/02	17
Ludwigshafen	10/18/02	<10
Bensheim	10/25/02	<10
Pfungstadt	10/25/02	<10
Gernsheim	05/27/03	<10
Mainz	10/18/02	43
Mainz	05/21/03	<10
Eltville	06/10/02	38
Koblenz	07/09/03	71
Leverkusen	11/27/02	31
Krefeld	05/07/03	<10
Wesel	05/08/03	<10
Emmerich	05/07/03	582
Hohenmoelsen	06/13/02	140
Hohenmoelsen	11/19/02	112
Schkopau	11/19/02	63
Halle	11/19/02	<10
Merseburg	11/18/02	76
Naumburg	11/18/02	<10
Leuna	11/18/02	712
Spergau	11/18/02	608
Weissenfels	11/18/02	<10
Bad Duerrenberg	11/18/02	76
Reichardtswerben	11/19/02	<10

Table A2: River Lippe and Wesel-Datteln-Canal

Sampling Date	Location	MTBE [ng/L] Lippe	MTBE [ng/L] Wesel-Datteln-Canal	Benzene [ng/L] Lippe
05/08/03	L1,WDC1	274	269	10
05/08/03	L2,WDC2	87	133	10
05/08/03	L3,WDC3	369	130	2005
05/08/03	L4,WDC4	318	68	1099
05/08/03	L5,WDC5	296	176	766
05/08/03	L6,WDC6	266	161	642
05/08/03	L7,WDC7	180	75	398
05/08/03	L8,WDC8	131	142	214
05/07/03	L9,WDC9	453	93	168

Table A3: River Saale

Sampling Date	Location	MTBE [ng/L]
11/18/02	S1	45
11/18/02	S2	10
11/18/02	S3	29
11/18/02	S4	19
11/18/02	S5	13
11/18/02	S6	384
11/18/02	S7	387
11/19/02	S8	320
11/19/02	S9	381
11/19/02	S10	377
11/19/02	S11	374

Table A4: River Rhine

Sampling Date	Location	MTBE [ng/l]	Sampling Date	Location	MTBE [ng/l]
08/16/02	R1	76	05/07/03	Duesseldorf	252
08/16/02	R2 left bank	88	05/07/03	Krefeld	161
08/16/02	R3	73	05/07/03	Duisburg	167
08/16/02	R4	5421	05/07/03	Mehrum/Voerde, R12	497
08/16/02	R5 oil harbor	991	05/07/03	Wesel, R 13	272
08/16/02	R6	1375	05/07/03	Wesel, R 14	292
08/16/02	R7	939	05/07/03	Bislich	250
08/16/02	R8 left bank	67	05/07/03	Emmerich	170
08/16/02	R9	488			
08/16/02	R10	407			
08/16/02	R11	328			

Table A5: Snow Samples

Sampling Date	Location	MTBE [ng/L]
01/19-20/02	Frankfurt/M-City	30
02/09/02	Frankfurt/M-Schwanheim	113
02/09/02	Frankfurt/M-Sossenheim	108
02/09/02	Frankfurt/M-Lohrberg	127
02/22/02	Frankfurt/M-City	42
03/14/02	Frankfurt/M-City	54
01/13/03	Frankfurt/M-City	16
12/23/01	Endingen	43
12/19-20/01	Endingen	174
11/23/01	Homberg/O	47
11/23/01	Homberg/O	<10
02/09/02	Dammbach	120
02/09/02	Sourbrodt/Hohes Venn (B)	75
12/19/01	Kleiner Feldberg/Ts	78
02/09/02	Kleiner Feldberg/Ts	111
02/18-19/02	Kleiner Feldberg/Ts	247
02/20-21/02	Kleiner Feldberg/Ts	<10
01/06-07/03	Kleiner Feldberg/Ts	155
01/30-31/03	Kleiner Feldberg/Ts	61
02/03-04/03	Kleiner Feldberg/Ts	37
02/04-05/03	Kleiner Feldberg/Ts	11
02/05-06/03	Kleiner Feldberg/Ts	33
12/16-17/02	Schmücke	438
01/13-14/03	Schmücke	631
12/16-17/02	Brotjacklriegel	126
12/31/02-01/01/03	Brotjacklriegel	<10
01/14-15/03	Brotjacklriegel	<10
01/31/03-02/01/03	Brotjacklriegel	<10
01/03/02	Kandel *	21
01/06/03	Schauinsland	91
01/13/03	Schauinsland	42
01/16/03	Schauinsland	17
01/19/03	Schauinsland	<10
01/03/02	Kandel	222
04/05/02	Kl. Scheidegg (CH)	<10
04/05/02	Kl. Scheidegg (CH)	<10
04/22/03	Zugspitze	<10
04/22/03	Zugspitze	<10
04/05/02	Jungfraujoch (CH)	<10
04/05/02	Jungfraujoch (CH)	<10
04/05/02	Jungfraujoch (CH)	<10
04/05/02	Jungfraujoch-Sphinx (CH)	<10
04/05/02	Jungfraujoch (CH)	<10

Table A6: Groundwater (contaminated sites)

Sampling Date	Location	MTBE [ng/l]
04/04/01	Site 1	42720000
09/13/01	Site 1	263
09/13/01	Site 1	100091
09/13/01	Site 1	5172
09/13/01	Site 1	100300
09/13/01	Site 1	41900000
09/13/01	Site 1	299
04/04/00	Duesseldorf	56
04/04/00	Duesseldorf	62420
04/04/00	Duesseldorf	37244
04/04/00	Duesseldorf	77
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	756
04/04/00	Duesseldorf	152
04/04/00	Duesseldorf	8761
04/04/00	Duesseldorf	12305
04/04/00	Duesseldorf	569
04/04/00	Duesseldorf	2692
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	1400
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	1252
04/04/00	Duesseldorf	<10
04/04/00	Duesseldorf	1318
04/04/00	Duesseldorf	1368

Table A7: Groundwater (non-urban wells)

Sampling Date	Location (well no.)	MTBE [ng/l]
12/01/00	M12	<10
12/01/00	Br Va	1735
12/01/00	Br III	<10
12/01/00	Br II	<10
12/01/00	Br I	2149
12/01/00	M3	<10
11/29/00	GWM 8	<10
11/29/00	GWM 3	<10
11/29/00	GWM 9	<10
11/29/00	GWM 2	<10
11/29/00	GWM 1	629
11/29/00	GWM 7	<10
11/29/00	GWM 6	<10
11/29/00	GWM 15	<10
12/05/00	M VII	<10
12/05/00	M IV	<10
12/05/00	M 9	<10
12/05/00	GWM 4	<10
12/01/00	M 7	<10
12/01/00	M 8	<10
02/27/01	Br. Va	<10
02/27/01	Br. I	34
02/27/01	Br. VI	17
02/27/01	Br. IV	<10
02/27/01	Br. V	<10
02/27/01	GWM1	<10
02/27/01	Sammelbehaelter	75
02/27/01	BFT-Erlensee	628
02/27/01	Im Weiherts	<10
02/27/01	Weihertsweg	377
02/27/01	Langenselbold Zulauf	131
02/27/01	Langenselbold Ablauf	117
03/16/01	BFU Baugrube	99
04/04/01	Bez. Fritz-Hamm Brunnen	<10
04/04/01	Bez.Koenig Heinrich Brunnen	<10
04/04/01	Bez. Trinkbrunnen 2	<10
04/04/01	Bez. Trinkbrunnen 1	<10
08/14/01	Gewinnungsanlage Eidengesaess Quelle 1+2	<10
08/14/01	MKK Mischwasser Quellen Rosengarten	<10
08/14/01	Brunnen Roth	177
08/14/01	Brunnen B Gettenbachtal	<10
08/14/01	Brunnen A Gettenbachtal	<10
08/14/01	Hailerer Aue Brunnen 2	<10
08/14/01	Brunnen Eschengraben Haitz	<10
08/14/01	Quelle Sandborn Haitz	<10
08/14/01	Hailerer Aue Brunnen 6	<10
08/14/01	Hailerer Aue Brunnen 1	<10
08/14/01	Haitz Brunnen Rausch	<10
08/14/01	Brunnen Heeg Haitz	<10
08/14/01	Hailerer Aue Brunnen 5	<10
08/14/01	Brunnen F Gettenbachtal	<10
08/14/01	Hailerer Aue Brunnen 4	<10
08/14/01	Brunnen Eidengesaess	<10
08/14/01	Gewinnungsanlage Eidengesaess Saarland Quelle	<10
08/14/01	Brunnen Bocksborn Haitz	<10
06/11/02	Weihertsweg	105
06/11/02	Im Weiherts	<10
06/11/02	Lache	1313
06/11/02	Im Weiherts (n. 240 min)	<10
11/19/02	Br II	<10
11/19/02	Br I	12
11/19/02	Br Va	<10
11/19/02	Br Mitte	800
11/19/02	Br Weihertsweg	132
11/19/02	Br V	<10

Table A8: Groundwater (urban wells)

Sampling Date	Location (well no.)	MTBE [ng/l]
03/02/01	H-13	52
03/02/01	H-15	114
03/02/01	H-18	22
03/02/01	H-29	24
03/18/02	HLUG 507014	22
03/18/02	HLUG 507007	222
03/19/02	HLUG 0024255	62
03/20/02	HLUG 527213	<10
03/20/02	HLUG 507168	69
03/20/02	HLUG 544040	1835
03/21/02	HLUG 1092001	2356
03/21/02	HLUG 507047	<10
03/18/02	HLUG 527120	26
02/20/02	City 1	<10
02/21/02	City 1	<10
02/19/02	City 1	39
02/19/02	City 1	<10
02/19/02	City 1	<10
02/19/02	City 1	95
02/21/02	City 1	<10
02/21/02	City 1	17
02/21/02	City 1	<10
02/21/02	City 1	<10
02/21/02	City 1	<10
02/20/02	City 1	15
02/20/02	City 1	<10
02/20/02	City 1	<10
02/20/02	City 1	35
02/20/02	City 1	99
02/20/02	City 1	36
02/20/02	City 1	40
02/20/02	City 1	<10
02/19/02	City 1	19
02/19/02	City 1	30
02/19/02	City 1	13
02/19/02	City 1	8236
02/19/02	City 1	<10
02/20/02	City 1	81
08/28/02	City 1	<10
08/28/02	City 1	71
08/28/02	City 1	276
08/28/02	City 1	34
08/28/02	City 1	23
08/28/02	City 1	111
08/28/02	City 1	118
08/28/02	City 1	6070
08/28/02	City 1	47600
11/18/99	Mainova 459	<10
11/18/99	Mainova1761	<10
11/18/99	Mainova 1123	52
11/18/99	Mainova 1184	77
11/18/99	Mainova 1128	12
11/18/99	Mainova 1132	<10
04/06/00	Mainova 1761	<10
04/06/00	Mainova 459	<10
04/06/00	Mainova1184	101
04/06/00	Mainova 1132	<10
04/06/00	Mainova 1128	13
04/06/00	Mainova 1123	37
01/31/01	Mainova 1128	40
01/31/01	Mainova 1123	131
01/31/01	Mainova 1184	80
01/31/01	Mainova 1132	<10
05/09/01	Mainova 1123	238
05/09/01	Mainova 1184	250

Table A9: River Main (Frankfurt am Main)

Sampling Date	MTBE [ng/l]	Sampling Date	MTBE [ng/l]
01/14/99	<10	02/13/01	182
04/21/99	13	02/21/01	308
05/26/99	116	03/01/01	66
06/23/99	33	04/03/01	29
07/27/99	51	05/04/01	61
08/20/99	19	06/05/01	118
10/15/99	33	07/23/01	336
11/01/99	40	08/16/01	459
11/18/99	95	09/25/01	76
12/08/99	<10	10/31/01	67
12/14/99	21	11/21/01	22
01/28/00	31	12/06/01	18
02/17/00	26	01/11/02	110
03/17/00	13	02/28/02	42
04/06/00	22	03/25/02	20
04/28/00	80	04/26/02	39
05/13/00	367	05/28/02	49
05/15/00	151	06/21/02	88
06/15/00	181	07/08/02	114
07/18/00	21	08/16/02	174
08/23/00	221	10/03/02	85
08/30/00	367	11/06/02	37
09/13/00	359	12/12/02	16
10/11/00	88	01/24/03	35
10/24/00	152	02/28/03	23
11/11/00	28	03/27/03	26
11/19/00	36	04/24/03	127
11/27/00	71	04/24/03	126
12/05/00	255	04/24/03	122
12/13/00	502	04/24/03	133
12/17/00	122	04/24/03	96
12/28/00	104	04/24/03	135
01/04/01	106	04/24/03	157
01/12/01	49	04/24/03	234
01/20/01	34	05/16/03	151
01/28/01	66	06/26/03	985
02/05/01	33	07/30/03	562

Table A10: Dutch Rivers

Sampling Date	Location	MTBE [ng/L]
07/25/02	Vecht, Maarsen	1023
07/21/02	Marina,Gouda	1161

Table A11: Precipitation (Frankfurt am Main)

Sampling Date	MTBE [ng/l]	Sampling Date	MTBE [ng/l]
12/07/98	53	01/05/01	24
12/15/98	70	01/10/01	12
03/22/99	<10	01/11/01	66
03/29/99	<10	01/24/01	40
06/10/99	<10	01/28/01	11
07/19/99	<10	02/03/01	23
08/18/99	13	02/06/01	12
09/23/99	16	02/07/01	13
10/01/99	21	02/13/01	74
11/20/99	29	02/22/01	70
12/15/99	40	02/28/01	<10
01/05/00	<10	03/01/01	64
02/01/00	<10	03/09/01	34
03/01/00	<10	03/12/01	<10
03/06/00	<10	03/13/01	<10
04/29/00	<10	05/16/01	<10
05/01/00	<10	06/17/01	26
05/17/00	<10	07/07/01	<10
06/22/00	<10	08/07/01	<10
07/01/00	<10	09/31/01	25
07/24/00	<10	10/21/01	33
08/19/00	<10	11/22/01	<10
09/06/00	34	01/20/02	30
09/13/00	<10	02/05/02	13
09/20/00	41	02/19/02	23
10/12/00	36	02/22/02	42
10/19/00	33	03/14/02	54
10/23/00	80	04/14/02	19
10/25/00	11	04/26/02	17
10/27/00	17	05/18/02	<10
10/31/00	<10	06/05/02	<10
11/01/00	85	07/01/02	<10
11/06/00	<10	08/20/02	14
11/13/00	45	10/03/02	<10
11/17/00	22	10/15/02	37
11/23/00	<10	11/07/02	81
12/05/00	31	12/15/02	92
12/12/00	14	01/13/03	16
12/14/00	<10	03/01/03	51
12/22/00	12	03/02/03	11
12/27/00	24	03/03/03	<10
12/28/00	43	04/22/03	28
01/02/01	75	04/29/03	<10
		05/13/03	<10
		06/18/03	<10
		07/24/03	<10

Table A12: Municipal Sewage Plant Effluents and Influents

Sampling Date	MTBE [ng/L] Effluent of Sewage Plant Niederrad	MTBE [ng/L] Influent Niederrad of Sewage Plant Niederrad	MTBE [ng/L] Influent Griesheim of Sewage Plant Niederrad
11/11/00	<10	181	32
11/19/00	14	140	24
11/27/00	76	137	70
12/05/00	255	709	138
12/13/00	642	170	63
12/17/00	104	74	51
12/28/00	78	1268	196
01/04/01	108	529	291
01/12/01	57	351	296
01/20/01	40	251	171
01/28/01	64	299	262
02/05/01	35	217	273
02/13/01	430	332	325
02/21/01	1229	748	524
03/01/01	829	353	494
03/09/01	377	1360	233
05/12/01	127	504	62
06/05/01	85	98	111
07/15/01	512	2436	10
08/16/01	50	10	149
09/25/01	291	1306	46
12/26/01	291	462	1049
01/11/02	3162	588	318
02/28/02	281	341	396
03/24/02	159	373	347
04/26/02	140	436	60
05/27/02	242	217	134
07/07/02	17	94	29
08/16/02	39	86	45
10/03/02	52	229	127
10/11/02	43	113	365
11/04/02	68	215	57
12/14/02	75	228	112
01/03/03	66	206	67
01/27/03	77	226	63
03/24/03	83	40	48
05/03/03	92	305	58
06/04/03	163	1181	108
07/30/03	108	256	99

Sampling Date	MTBE [ng/L] Effluent of Sewage Plant Sindlingen	MTBE [ng/L] Influent of Sewage Plant Sindlingen
11/11/00	--	47
11/19/00	--	133
11/27/00	--	21
12/05/00	--	136
12/13/00	--	46
12/17/00	--	30
12/28/00	--	277
01/04/01	--	277
01/12/01	--	211
01/20/01	--	362
01/28/01	--	87
02/05/01	--	86
02/13/01	356	574
02/21/01	81	96
03/01/01	55	88
03/09/01	90	140
05/12/01	10	28
06/05/01	10	<10
07/15/01	149	98
08/16/01	73	94
09/25/01	13	24
12/26/01	143	122
01/11/02	46	94
02/28/02	124	217
03/24/02	180	307
04/26/02	31	62
05/27/02	25	69
07/07/02	37	37
08/16/02	25	60
10/03/02	54	75
10/11/02	<10	22
11/04/02	35	70
12/14/02	193	297
01/03/03	34	57
01/27/03	26	66
03/24/03	126	50
05/03/03	18	45
06/04/03	73	88
07/30/03	86	233

Table A13: Industrial Effluents

Sampling Date	Company No.	MTBE [ng/l]
06/13/00	1	14
10/23/00	1	<10
08/23/00	2	<10
11/08/00	2	<10
01/25/01	2	12397
04/22/02	2	15
04/22/02	2	<10
08/24/00	3	<10
01/22/01	3	40
03/20/02	3	31
08/31/00	4	183
01/23/01	4	28422
08/31/00	4	173
03/19/02	4	558
03/19/02	4	61
08/30/00	5	53
01/25/01	5	49
04/29/02	5	<10
01/23/01	6	53
01/22/01	7	20
08/31/00	8	127
01/24/01	8	1814
01/24/01	8	<10
01/24/01	8	361
01/24/01	8	185
03/18/02	8	748
03/18/02	8	6610
03/18/02	8	35
03/18/02	8	5010
03/19/02	9	254
04/24/02	10	183
04/24/02	10	140
04/25/02	11	<10
04/25/02	11	21

PUBLICATIONS

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