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Occurrence, distribution and behavior of hydrophilic ethers in the aquatic environment

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Abstract

The objective of the present doctoral thesis was to investigate the occurrence, distribution, and behaviour of six hydrophilic ethers: ethyl *tert*-butyl ether (ETBE), 1,4-dioxane, ethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) in surface-, waste-, ground- and drinking water samples. Solid phase extraction and gas chromatography/mass spectrometry were used to analyze the six hydrophilic ethers. Altogether more than 150 surface water samples, almost 100 of each groundwater and wastewater samples, and 10 raw and drinking water samples were analyzed during the research project.

Initially, the method was validated in order to simultaneously determine the analytes of interest in various aquatic environments. A solid phase extraction method that uses coconut charcoal (Resprep® activated coconut charcoal, Restek) or carbon molecular sieve material (Supelclean™ Envi-Carb™ Plus, Supelco) for analyte absorption were found suitable for determination of ETBE, 1,4-dioxane, and glymes in surface-, drinking-, ground- and wastewater samples. Precision and accuracy of both methods was demonstrated for all analytes of interest. The recovery of target compounds from the ultrapure water spiked at 1.0 µg L^{-1} was between 86.8 % and 98.2 %, with relative standard deviation below 6 %. The samples spiked at 10.0 µg L^{-1} gave slightly higher recovery of 90.6 % to 112.2 % with a relative standard deviation below 3.4 % for each analyte. Detection and quantification limits in ultrapure water and surface waters were furthermore established. The limit of quantitation (LOQ) in ultrapure water ranged between 0.024 µg L^{-1} to 0.057 µg L^{-1} using Restek cartridges, and 0.030 µg L^{-1} to 0.069 µg L^{-1} using Supelco cartridges. In the surface water samples the calculated LOQ was 0.032 µg L^{-1} to 0.067µg L^{-1} using coconut charcoal material and 0.032 µg L^{-1} to 0.052 µg L^{-1} using the carbon molecular sieve material. Moreover, stability of the unpreserved and preserved water samples as well as the extracts was determined. Preservation of samples with sodium bisulfate (at 1 gram per Liter) resulted in much better stability of the ethers in water samples. Subsequently, 27 samples obtained from seven surface water bodies in Germany (Rivers Rhine, Lippe, Main, Oder, Rur, Schwarzbach and Wesel-Datteln Canal) were analyzed for the six hydrophilic ethers. ETBE was present in only two surface waters (Rhine River and Wesel-Datteln Canal) with concentrations close to the LOQ (up to 0.065 µg L^{-1}). 1,4-Dioxane was detected in all of the water samples at concentrations reaching 1.93 µg L^{-1}. Monoglyme was identified only in the Main and Rhine

Rivers at the maximum concentration of 0.114 µg L^{-1} and 0.427 µg L^{-1}, respectively. Very high concentrations (up to 1.73 µg L^{-1}) of diglyme, triglyme, and tetraglyme were detected in the samples from the Oder River. These glymes were also detected in the Rhine River; however the concentrations did not exceed 0.200 µg L^{-1}. Furthermore, tetraglyme was detected in the Main River at an average concentration of 0.409 µg L^{-1} (n = 6) and in one sample from the Rur River at 0.192 µg L^{-1}.

Four sampling campaigns were conducted at the Oderbruch polder between October 2009 and May 2012, in order to study the behavior of the hydrophilic ethers and organophosphates during riverbank filtration and in the anoxic aquifer. Moreover the suitability of these target compounds was assessed for their use as groundwater organic tracers. At the time of each sampling campaign, concentrations of triglyme and tetraglyme in the Oder River were between 20–185 ng L^{-1} (n = 4) and 273–1576 ng L^{-1} (n = 4). Monoglyme, diglyme, and 1,4-dioxane were analyzed only during the two last sampling campaigns. At that time, the concentration of diglyme in Oder River was 65–94 ng L^{-1} (n = 2) and 1,4-dioxane 1610–3290 ng L^{-1} (n = 2). In the drainage ditch, following bank filtration, concentrations of ethers ranged between 1090 ng L^{-1} and 1467 ng L^{-1} for 1,4-dioxane, 23ng L^{-1} and 41 ng L^{-1} for diglyme, 37 ng L^{-1} and 149 ng L^{-1} for triglyme, and 496 ng L^{-1} and 1403 ng L^{-1} for tetraglyme. In the anoxic aquifer, 1,4-dioxane showed the greatest persistence during the groundwater passage. At the distance of 1150 m from the river and an estimated groundwater age of 41.9 years, a concentration above 200 ng L^{-1} was detected. A positive correlation was found for the inorganic tracer chloride (Cl^{-}) with 1,4-dioxane and tetraglyme. Similarities in the behavior of Cl^{-} and the organic compound suggested that 1,4-dioxane and tetraglyme are controlled by the same hydraulic process and therefore can be used as additional tracers to study the dynamics of the groundwater system. These results show that high concentrations of ethers are present in the surface water and are not removed during bank filtration processes. Moreover, the hydrophilic ethers persist in the anoxic aquifer and little or no degradation is expected, supporting, their possible application as organic tracers.

A separate sampling project was conducted for 1,4-dioxane that focused primarily on its fate in the aquatic environment. This study provided missing information on the extent of water pollution with 1,4-dioxane is Germany. Numerous waste-, surface-, ground- and drinking water samples were collected in order to determine the persistence of 1,4-dioxane in the aquatic environment. The occurrence of 1,4-dioxane was determined in wastewater samples from four municipal sewage treatment plants (STP). The influent and effluent samples were collected during weekly campaigns. The average influent concentrations in all four plants ranged from 262 ± 32 ng L^{-1} to 834 ± 480 ng L^{-1}, whereas the average effluents concentrations were between 267 ± 35 ng L^{-1} and 62,260 ± 36,000 ng L^{-1}. The source of increased 1,4-dioxane concentrations in one of the effluents was identified to originate from impurities in the methanol used in the postanoxic denitrification process. Spatial and temporal distribution of 1,4-dioxane in the river Main, Rhine, and Oder was also examined. Concentrations reaching 2,200 ng L^{-1} in the Oder River, and 860 ng L^{-1} in both Main and Rhine River were detected. The average load during the sampling was estimated to be 6.5 kg d^{-1} in the Main, 34.1 kg d^{-1} in the Oder, and 134.5 kg d^{-1} in the Rhine River. In all of the sampled rivers, concentrations of 1,4-dioxane increased with distance from the mouth of the river and were found to negatively correlate with the discharge of the river. In order to determine if 1,4-dioxane can reach drinking water supplies, samples from a Rhine River bank filtration site and potable water from two drinking water production facilities were analyzed for the presence of 1,4-dioxane in the raw water and finished potable water. The raw water (following bank filtration) contained 650 ng L^{-1} to 670 ng L^{-1} of 1,4-dioxane, whereas the concentration in the finished drinking water fell only to 600 ng L^{-1} and 490 ng L^{-1}, respectively.

During the final project, investigations of the source identification of high glyme concentrations in the Oder River were carried out. During four sampling campaigns between January, 2012 and April, 2013, 50 samples from the Oder River in the Oderbruch region and Poland were collected. During the first two samplings in the Oderbruch polder, glymes were detected at concentration reaching 0.07 µg L^{-1} (diglyme), 0.54 µg L^{-1} (triglyme) and 1.73 µg L^{-1} (tetraglyme) in the Oder River. The extensive sampling campaign of the Oder River (about 500 km) in Poland helped to identify the area of possible glyme entry into the river. During that sampling the maximum concentrations of triglyme and tetraglyme were 0.46 µg L^{-1} and 2.21 µg L^{-1}, respectively. A closer investigation of the identified area of pollution, helped to determine the possible sources of glymes in the Oder River. Hence, the final sampling focused on the Kaczawa River, a left tributary of the Oder River and Czarna Woda, a left tributary of Kaczawa River. Moreover, samples from an industrial wastewater treatment plant were collected. Samples from Czarna Woda stream and Kaczawa River contained even higher concentrations of diglyme, triglyme, and tetraglyme, reaching 5.18 µg L^{-1}, 12.87 µg L^{-1} and 80.81 µg L^{-1}, respectively. Finally, three water samples from a wastewater treatment plant receiving influents from a copper smelter were analyzed. Diglyme, triglyme, and tetraglyme were present at an average concentration of 569 µg L^{-1}, 4300 µg L^{-1}, and 65900 µg L^{-1}, respectively in the wastewater. Further research helped to identify the source of the glymes in the wastewater. The gas desulfurization process – Solinox implemented in the nearby copper smelter uses glymes as physical absorption medium for sulfur dioxide.

Results of this doctoral research provide important information about the occurrence, distribution, and behavior of hydrophilic ethers: 1,4-dioxane, monoglyme, diglyme, triglyme, and tetraglyme in the aquatic environment. A method capable of analyzing a wide range of ether compounds: from a volatile ETBE to a high molecular weight tetraglyme was validated. 1,4-Dioxane and tetraglyme were found to be applicable as organic tracers, since they are not easily attenuated during bank filtration and the anoxic groundwater passage. The extent of water pollution with 1,4-dioxane was shown in waste-, surface-, ground-, and drinking waters. One source of extremely high concentrations of 1,4-dioxane in a municipal sewage treatment plant applying postanoxic denitrification was identified, however more information is needed on the entry of 1,4-dioxane into surface waters. Moreover, 1,4-dioxane was present in drinking water samples from river bank filtration, which demonstrates its persistence in the aquatic environment and its low degradation potential during bank filtration and subsequent water treatment. Furthermore, this was the first study that focused primarily on identifying sources of glymes in surface waters. Glymes find a widespread use in industrial sectors, hence establishing their origin in the surface water is difficult (as with 1,4-dioxane). In this work, a gas desulphurization process was identified to be a dominating source of glyme pollution in the Oder River.

Keywords: 1,4-dioxane; glymes; bank filtration; drinking water; surface water; GC/MS; solid phase extraction

Zusammenfassung

Im Fokus der vorliegenden Dissertationsschrift stehen die sechs hydrophilen Ether: Ethyl-*tert*-butylether (ETBE), 1,4-Dioxan, Ethylenglycol-dimethylether (Monoglyme), Diethylenglycol-dimethylether (Diglyme), Triethylenglycol-dimethylether (Triglyme), und Tetraethylenglycol-dimethylether (Tetraglyme). ETBE ist ein Additiv für Vergaserkraftstoffe, das in vielen Ländern als Antiklopfmittel zum Einsatz kommt (z.B. Ersatz für MTBE). Des Weiteren verbessert ETBE die Verbrennung des Kraftstoffs, so dass die Emissionen von Kohlenwasserstoffen und Kohlenmonoxid durch die Kraftfahrzeuge verringert werden. 1,4-Dioxan wird größtenteils als Lösungsmittel bei der Produktion von Klebstoff, Abbeizmitteln, Farbstoffen, Entfettern, Gewebereinigern, Papier, Elektronik, aber auch bei vielen anderen Erzeugnissen verwendet (Sei et al., 2010). Es entsteht auch als unerwünschtes Nebenprodukt in industriellen Fertigungen, wie z.B. bei der Synthese von Polyester oder bei der Herstellung von Tensiden (Sei et al., 2010; Black et al., 2001). Glycoldimethylether (Glymes) sind gesättigte Polyether und werden üblicherweise als Reaktionslösungsmittel in der Pharmaindustrie verwendet, sowie bei der Herstellung von Spezialchemikalien. Zusätzlich sind Glymes in vielen fertigungstechnischen Produkten, wie z.B. in Druckfarben, Lackfarben, Beschichtungen, Klebstoffen, Batterien und Bremsflüssigkeiten, enthalten (U.S. Environmental Protection Agency, 2011). Die höhermolekularen Glymes, wie z.B. Tetraglyme, kommen auch als physikalische Absorptionslösungsmittel für die Entfernung von SO_2 und H_2S aus Abgasen, z.B. im sogenannten Solinox-Prozess, zum Einsatz. Die derzeitigen Produktionsvolumina, sowie die Verwendungen von den oben genannten Analyten, sind innerhalb Europas nicht bekannt. Bis 1995 wurde 1,4-Dioxan meist als Stabilisator für 1,1,1-Trichlorethan (1,1,1-TCE) genutzt. Da sich jedoch herausgestellt hat, dass 1,1,1-TCE die Ozonschicht angreift, wurde die Substanz mit dem „Montreal Protocol“ strenger reguliert (Doherty, 2000). Im Jahr 1997 lag das Produktionsvolumen von 1,4-Dioxan bei 2.000 – 2.500 Tonnen (European Commission, 2002). Gemäß der „Organization for Economic Cooperation and Development“ und der „European Chemical Substances Information System“ übersteigt die jährliche Produktion von Monoglyme und Diglyme 1.000 Tonnen pro Jahr in mindestens einem der EU-Mitgliedsstaaten (European Chemicals Agency, 2011a, 2011b). Im Jahre 2002 hat die „Oxygenated Solvent Producer Association“ Produktionszahlen von Triglyme von insgesamt über 1.000 Tonnen in Europa ermittelt (European Chemicals Agency, 2011c). In den letzten Jahren ist die Frage nach der

allgegenwärtigen Präsenz von 1,4-Dioxan in der Umwelt gestiegen und auch das Interesse an damit verbundenen gesundheitsschädlichen Auswirkungen. Die „United States Environmental Protection Agency“(U.S. EPA) und die „International Agency for Research on Cancer“ haben 1,4-Dioxan als „Probable Human Carcinogen“ (B2) eingestuft. Monoglyme, Diglyme und Triglyme wiesen klar auf Fortpflanzungs- und Entwicklungsstörungen bei Versuchstieren hin (Hardin, 1983; George et al., 1987; Schwetz et al., 1992; ECETOC, 2005). Wenn Menschen diesen Glymes ausgesetzt sind, könnte dies auch zur Unfruchtbarkeit und zu Schäden bei Schwangerschaften führen (EPA, 2011).

Die in dieser Studie betrachteten Ether haben eine moderate bis hohe Wasserlöslichkeit und besitzen Henry-Koeffizienten zwischen $1{,}04 \times 10^{-14}$ bis $1{,}64 \times 10^{-3}$ $\text{atm} \times \text{m}^3 \times \text{mol}^{-1}$ (Tetraglyme und entsprechend ETBE) und gewährleisten somit eine geringe Volatilität aus wässrigen Lösungen. Basierend auf dem n-Octanol-Wasser-Verteilungskoeffizienten ($\log P_{\text{ow}} = -1.03$ bis 1.92) haben sie ein vernachlässigbares Potential zur Bioakkumulation. Der relativ hohe Dampfdruck (< 0.01 bis 124 mm Hg) ermöglicht eine schnelle Verdampfung aus trockenen Böden. Aufgrund ihrer physikochemischen Eigenschaften belasten die Substanzen insbesondere die aquatische Umwelt und implizieren dadurch eine schwierige Entfernung aus dem Wasser. Dieses Problem erhöht die Wahrscheinlichkeit für eine mögliche Verunreinigung von Oberflächen- und Grundwasser.

Keine der oben genannten Zielsubstanzen wurde in den europäischen Gewässern bezüglich ihrer Verbreitung umfangreich geprüft. Der Großteil der Forschungen war auf das Kraftstoffadditiv Methyl-*tert*-butylether (MTBE) fokussiert. Die Verbreitung von ETBE in der Umwelt wurde dagegen deutlich weniger erforscht und die Substanz wurde nur sporadisch im Wassersystem nachgewiesen, obwohl die Nutzung von ETBE in vielen europäischen Ländern weit verbreitet ist (Rosell et al., 2003; van Wezel et al., 2009; LUBW, 2010; Fayolle-Guichard et al., 2012; Stupp et al., 2012; IAWR, 2013). Zum Vorkommen von 1,4-Dioxan in Oberflächen-, Grund-, und Trinkwasser wurden ebenfalls nur wenige Informationen, vorwiegend aus den U.S.A. und Japan, veröffentlicht. In einem Auswertungsreport der europäischen Union wurden in den Niederlanden 0,5 $\mu\text{g l}^{-1}$ 1,4-Dioxan im Trinkwasser und zwischen 1 und 10 $\mu\text{g l}^{-1}$ im Oberflächenwasser nachgewiesen (European Commission, 2002). 1,4-Dioxan ist auch ein Nebenprodukt bei der Herstellung von Kosmetika. Aus diesem Grund hat das Chemische und Veterinäruntersuchungsamt von Karlsruhe und Freiburg mehrere Shampoos, Dusch- und

Schaumbäder getestet. Hier wurde eine Durchschnittskonzentration von 1,4-Dioxan zwischen 1 und 2 ppm (mg kg^{-1}) bestimmt. In Deutschland wurde 1988 der Grenzwert für 1,4-Dioxan in kosmetischen Fertigerzeugnissen auf 10 ppm festgelegt. Auch wenn die für Fertigerzeugnisse festgesetzten Grenzwerte bei den Untersuchungen erreicht worden sind, ist es das Ziel, die Menge an 1,4-Dioxan in Körperpflegeprodukten weiter zu reduzieren. Vakkuumstrippen wurde von der US EPA als ein Verfahren vorgeschlagen, bei dem man 1,4-Dioxan aus industriellen Abläufen entfernen kann. Glymes standen nur selten im Fokus der Umweltforschungen. Nachdem hohe Konzentrationen von Diglyme, Triglyme und Tetraglyme im Jahr 2005 im Rhein nachgewiesen worden waren, wurden in der Folgezeit die Konzentrationen im Rhein von der internationalen Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet (IAWR) kontinuierlich überprüft. Dennoch wurde die ursprüngliche Quelle dieser Kontaminationen der Substanzen im Rhein nie genau belegt.

Das Ziel dieser Dissertation ist es, die Wissenslücken im Bezug auf das Vorkommen, die Verteilungen und die Eintragsquellen von ETBE, 1,4-Dioxan und Glymes in ausgewählten europäischen Gewässern zu schließen. Im Rahmen der Dissertation sollten die folgenden Fragen geklärt werden:

- Existiert eine Methode welche die gleichzeitige Bestimmung von den oben genannten Analyten ermöglicht und kann diese für verschiedene Wasserproben validiert werden?
- Wie hoch sind die Konzentrationen der untersuchten Ether in den bedeutenden Fließgewässern in Deutschland und Polen?
- Können ETBE, 1,4-Dioxan und Glymes in anoxischem Grundwasser, welches durch Infiltration von Flusswasser geprägt ist, nachgewiesen werden?
- Sind die untersuchten hydrophilen Ether als organische Tracer nutzbar?
- Wie ist die räumliche und zeitliche Verteilung von 1,4-Dioxan in bedeutenden Flüssen Deutschlands und Polens?
- Wie hoch ist die Durchschnittsbelastung von 1,4-Dioxan in den untersuchten Fließgewässern?
- Kann 1,4-Dioxan in den regionalen Abwasserreinigungsanlagen nachgewiesen werden, und kann es wieder aus dem Wasser abgebaut werden?
- Können Eintragsquellen von 1,4-Dioxan in kommunalen Kläranlagen identifiziert werden?

- Kann ein Abbau von 1,4-Dioxan während der Uferfiltration und bei der Trinkwasseraufbereitung festgestellt werden?
- Wie ist die räumliche Verteilung von Diglyme, Triglyme und Tetraglyme in der Oder?
- Lassen sich Punktquellen für Glymes in Fließgewässern identifizieren?

Am Anfang des Forschungsprojekts wurde die Methode für die simultane Bestimmung der genannten Analyten in wässrigen Proben validiert. Für Oberflächen-, Trink-, Grund-, und Abwasserproben ist eine Festphasenextraktion verwendet worden, bei der Kokosnussholzkohle (Resprep® activated coconut charcoal, Restek) oder „Carbon Molecular Sieve Material“ (Supelclean™ ENVI-Carb™ Plus, Supelco) zum Einsatz kamen. Um die Analyten im Nano- und Mikrogrammbereich pro Liter zu quantifizieren, wurden Standards und Proben mit Gaschromatographie gekoppelt an Massenspektrometrie im SIM-Modus (SIM = selected ion monitoring) unter Verwendung der jeweils relevanten Massenspur analysiert. Die Bestimmungsgrenzen (Limit of quantitation-LOQ) für ETBE, 1,4-Dioxan, Monoglyme, Diglyme, Triglyme und Tetraglyme in verschiedenen Wassermatrizen wurden für beide Methoden berechnet. Die Methode, bei der Restek Kartuschen und 500 ml jeder Wasserprobe eingesetzt werden, hat die folgenden Bestimmungsobergrenzen für ETBE, 1,4-Dioxan, Monoglyme, Diglyme, Triglyme und Tetraglyme: 0,044 µg l^{-1}, 0,034 µg l^{-1}, 0,024 µg l^{-1}, 0,047 µg l^{-1}, 0,055 µg l^{-1}, 0,057 µg l^{-1} in Reinstwasser und 0,067µg l^{-1}, 0,052µg l^{-1}, 0,032 µg l^{-1}, 0,044 µg l^{-1}, 0,035 µg l^{-1}, 0,041 µg l^{-1} entsprechend in Oberflächenwasser. Die Methode mit den Kartuschen Supelclean™ ENVI-Carb™ Plus ergaben LOQs von 0,034 µg l^{-1} für 1,4-Dioxan, 0,030 µg l^{-1} für Monoglyme, 0,067 µg l^{-1} für Diglyme, 0,069 µg l^{-1} für Triglyme und 0,067 µg l^{-1} für Tetraglyme in Reinstwasser. Die LOQs für 1,4-Dioxan, Monoglyme, Diglyme, Triglyme und Tetraglyme in Oberflächenwasser wurden entsprechend mit 0,052 µg l^{-1}, 0,035 µg l^{-1}, 0,032 µg l^{-1}, 0,044 µg l^{-1}, und 0,047 µg l^{-1} berechnet.

Zu Beginn der Untersuchung wurden 27 Proben von sieben verschiedenen Fließgewässern innerhalb Deutschlands genommen (Rhein, Lippe, Main, Oder, Rur, Schwarzbach und Wesel-Datteln-Kanal), um darin die sechs hydrophilen Ether zu analysieren. ETBE konnte nur im Rhein und im Wesel-Datteln-Kanal mit Konzentrationen nahe der Bestimmungsgrenze (bis zu 0,065 µg l^{-1}) gefunden werden. 1,4-Dioxan wurde mit Konzentrationen bis zu 1,93 µg l^{-1} in allen Wasserproben nachgewiesen. Monoglyme war nur im Main mit Konzentrationen bis zu 0,114 µg l^{-1} und im Rhein mit bis zu 0,427 µg l^{-1} zu finden. Sehr hohe Konzentrationen (bis zu 1,73 µg

l^{-1}) von Diglyme, Triglyme und Tetraglyme wurden in der Oder identifiziert. Darüber hinaus konnten diese Glymes auch im Rhein nachgewiesen werden, dort aber nur mit Konzentrationen bis zu 0,200 µg l^{-1}. Tetraglyme ist auch im Main mit Durchschnittskonzentrationen von 0,409 µg l^{-1} (n=6) bestimmt worden und mit nur 0,192 µg l^{-1} in einer Probe der Rur.

Vier Probenahmekampagnen wurden an der Oder und am Grundwasser des Oderbruchs zwischen Oktober 2009 und Mai 2012 vollzogen. Dort wurde das Vorkommen und Verhalten von hydrophilen Ethern und Phosphorsäureestern während der Uferfiltration und im Grundwasser untersucht, um ihre Eignung als organische Tracer zu überprüfen. Alle Proben der Oder zeigten Konzentrationen von Triglyme und Tetraglyme, die zwischen 20 bis 185 ng l^{-1} (n = 4) und 273 bis 1576 ng l^{-1} (n = 4) lagen. Die anderen Ether wurden nur in den zwei letzten Probenahmen mit Konzentrationen von 65 bis 94 ng l^{-1} (n = 2) für Diglyme und von 1610 bis 3290 ng l^{-1} (n = 2) für 1,4-Dioxan nachgewiesen. Im Entwässerungsgraben nach der Uferfiltration lagen die Konzentrationen bei 1,4-Dioxan zwischen 1090 ng l^{-1} und 1467 ng l^{-1}, bei Monoglyme zwischen 23 ng l^{-1} und 41 ng l^{-1}, bei Triglyme zwischen 37 ng l^{-1} und 149 ng l^{-1} und bei Tetraglyme zwischen 496 ng l^{-1} und 1403 ng l^{-1}. Im anoxischen Aquifer zeigte 1,4-Dioxan die größte Persistenz in der Grundwasserpassage. Bei einer Entfernung von 1150 m vom Fluss und einem geschätzten Alter des Grundwassers von 41,9 Jahren wurde noch eine Konzentration von über 200 ng l^{-1} gefunden. Der anorganische Tracer Chlorid (Cl^{-}) korrelierte positiv mit 1,4-Dioxan und Tetraglyme. Ein ähnliches Verhalten von Cl^{-} und organischen Substanzen deuten darauf hin, dass 1,4-Dioxan und Tetraglyme durch die gleichen hydraulischen Vorgänge beeinflusst werden und daher auch als zusätzliche Tracer zur Studie der Dynamik des Grundwassersystems benutzt werden können. Die Ergebnisse zeigen, dass hohe Konzentrationen von Ethern im Oberflächenwasser vorhanden sind und dass diese während der Uferfiltration nicht abgebaut werden. Des Weiteren werden die hydrophilen Ether im anoxischen Aquifer aufgrund ihrer geringen Octanol-Wasser-Verteilungskoeffzienten nicht retardiert, so dass sie ein hohes Potential für die Verwendung als organische Tracer aufweisen.

In einem weiteren Teilprojekt wurde das Vorkommen von 1,4-Dioxan in der aquatischen Umwelt untersucht. Diese Studie sollte fehlende Informationen bezüglich der Verunreinigung verschiedener Kompartimente der aquatischen Umwelt mit 1,4-Dioxan in Deutschland liefern. Dazu wurden insgesamt über 220 Proben von Grund-, Trink-, Ab- und Oberflächenwasser gesammelt, um genauere Informationen über die vermeintliche Persistenz von 1,4-Dioxan in der aquatischen Umwelt zu gewinnen. 1,4-Dioxan wurde in den Zu- und Abläufen von vier Kläranlagen in stark schwankenden Konzentrationen nachgewiesen. Die Zu- und Abläufe der Kläranlagen wurden in vier jeweils wöchentlichen Probenahmekampagnen beprobt. Die Mittelwerte der Konzentrationen der Zulaufproben der vier Kläranlagen lagen zwischen 262 ± 32 ng l^{-1} und 834 ± 480 ng l^{-1}, wohingegen die Mittelwerte der Konzentrationen in den Ablaufproben zwischen 267 ± 35 ng l^{-1} und 62,260 ± 36,000 ng l^{-1} lagen. Als Quelle für die stark erhöhte 1,4-Dioxan-Konzentration im Ablauf einer Kläranlage wurde verunreinigtes Methanol identifiziert, welches in der nachgeschalteten Denitrifikation dieser Kläranlagen als Kohlenstoffquelle für die Denitrifikanten zum Einsatz kam. Weiterhin wurde die räumliche und zeitliche Verbreitung von 1,4-Dioxan im Rhein, Main und in der Oder untersucht. Es wurden Konzentrationen bis zu 2200 ng l^{-1} in der Oder und bis zu 860 ng l^{-1} im Rhein und im Main bestimmt. In allen Flüssen ist die Konzentration von 1,4-Dioxan bei jeder Probenahme flussabwärts in Richtung Mündung tendenziell gestiegen. Bei der zweiwöchigen Untersuchung an der Rheingütestation Worms wurde festgestellt, dass die Konzentrationen von 1,4-Dioxan negativ mit der Abflussmenge des Flusses korrelieren. Die Studien an Rhein, Oder und Main ergaben eine Durchschnittsfracht an 1,4-Dioxan von 134,5 kg d^{-1}, 34,1 kg d^{-1}, und 6,5 kg d^{-1}. Zusätzlich wurden auch Uferfiltrations- und Trinkwasserproben von zwei Trinkwasseranlagen auf 1,4-Dioxan getestet. Das Rohwasser enthielt 650 ng l^{-1} bis 670 ng l^{-1} 1,4-Dioxan, wohingegen die Konzentrationen im Trinkwasser nur auf 600 ng l^{-1} in der ersten und auf 490 ng l^{-1} in der zweiten Anlage zurückgingen.

Zum Abschluss wurde noch nach der Quelle für die hohen Konzentrationen der Glymes in der Oder gesucht. Dazu wurden vier Probenahmekampagnen in der Region im Bereich des Oderbruchs und in Polen durchgeführt. Die ersten zwei Probenahmen ergaben Konzentrationen von Glymes in der Region um den Oderbruch von 0,07 µg l^{-1} (Diglyme), 0,54 µg l^{-1} (Triglyme) und 1,73 µg l^{-1} (Tetraglyme). Die anschließenden ausgiebigen Probenentnahmen an der Oder in Polen konnten zunächst den Eintrittsbereich der Glymes in die Oder eingrenzen und einen Nebenfluss (Kaczawa) der Oder als Quelle für die Glymes in der Oder deutlich machen. Die Proben aus der Oder (unmittelbar hinter der Mündung der Kaczawa in die Oder) ergaben maximale Konzentrationen von Triglyme mit 0,46 µg l^{-1} und von Tetraglyme mit 2,21 µg l^{-1}. Bei der Probenahme wurde der Einzugsbereich dieses Nebenflusses näher untersucht. Proben der Flüsse Czarna Woda und Kaczawa lieferten dabei sogar noch höhere Konzentrationen von Diglyme, Triglyme, und Tetraglyme mit Werten von 5,18 µg l^{-1}, 12,87 µg l^{-1} bzw. 80,81 µg l^{-1}, wodurch die Quelle weiter eingegrenzt werden konnte. Diese wurde schließlich als der Ablauf einer Kläranlage, welche die Abwässer einer Kupferhütte reinigt, identifiziert. Diglyme, Triglyme und Tetraglyme wurden mit mittleren Konzentrationen (n = 3) von 569 µg l^{-1}, 4300 µg l^{-1} und 65900 µg l^{-1} im Abwasser bestimmt. Weitere Nachforschungen konnten die Bezugsquelle der Glymes im Abwasser identifizieren. Die Gasentschwefelungsanlage (Solinox) in der Kupferhütte benutzt Glymes als physikalisches Absorptionsmittel für Schwefeldioxid aus den Rauchgasen und ist somit für die hohen Konzentrationen der Glymes im Ablauf der Kläranlage verantwortlich, die das Abwasser der Kupferhütte reinigt.

Die Ergebnisse aus dieser Dissertationsschrift zeigen zusammenfassend, dass die Konzentrationen von ETBE in den untersuchten Proben durchweg sehr gering sind (bis zu 0,065 µg l^{-1}). Dies ist damit erklärbar, dass die Nutzung von ETBE als Kraftstoffzusatz aufgrund der Substitution durch Ethanol deutlich zurückgegangen ist. Derzeit sind Mischungen von Ethanol/Bioethanol mit Vergaserkraftstoffen allgemein üblich und gelangen als Kraftstoffe mit den Bezeichnungen E5, E10, E85 auf den Markt. Die ermittelten hohen Konzentrationen von 1,4-Dioxan in unserer aquatischen Umwelt bis hin zum Trinkwasser sind besorgniserregend und erfordern dringenden Handlungsbedarf. Als eine bedeutende Quelle für 1,4-Dioxan im Main konnte der Ablauf einer Kläranlage identifiziert werden, die ein mit 1,4-Dioxan verunreinigtes Methanol als Kohlenstoffquelle für die nachgeschaltete Denitrifikation einsetzt. Für die hohen Frachten an 1,4-Dioxan in unseren Flüssen müssen darüber hinaus zahlreiche bisher noch unbekannte Eintragsquellen vorhanden sein. Weitere Anschlussprojekte sind deshalb zur Identifizierung dieser Quellen erforderlich. Besonders bedenklich ist die Tatsache, dass 1,4-Dioxan die Uferfitration und die Trinkwasseraufbereitung nahezu ohne Konzentrationsverringerung übersteht. Auch bezüglich der Tri- und Tetraglymes konnte eine gravierende Kontaminationsquelle identifiziert werden. Diese kommt dadurch zustande, dass es offenbar problematisch ist, die z.B. im Solinox-Verfahren als Absorptionsmedium für Schwefeloxidgase eingesetzten Glymes bei der Aufbereitung vollständig zu entfernen, und dass diese dadurch zum Teil in das Abwasser gelangen. Da das Solinox-Verfahren nicht nur bei der Kupferverhüttung in Polen, sondern vielerorts in Europa zum Einsatz kommt, besteht Bedarf auch an diesen Standorten eine mögliche Belastung der Abwässer mit Glymes zu untersuchen.

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Dziękuję bardzo, Thank you very much, Danke schön!

Acronyms

1,1,1-TCA	1,1,1-Trichloroethane
AOP	Advanced oxidation processes
BDL	Below detection limit
CAS	Chemical abstracts service
DCM	Dichloromethane
Diglyme	Diethylene glycol dimethyl ether
DIN	German Institute of Standardizations
DOC	Dissolved organic carbon
DWT	Drinking water treatment plant
ECETOC	European centre for ecotoxicology and toxicology of chemicals
ECSIS	European chemical substances information system
EFRA	European flame retardant association
ETBE	Ethyl *tert*-butyl ether
EU	European Union
FGD	Flue gas desulfurization
GC	Gas chromatography
IARC	International agency for research on cancer
IAWR	International association of water works in the Rhine
IS	Internal standard
IUCLID	International uniform chemical information database
LOD	Limit of detection (same as MDL)
Log P_{ow}	*n*-octanol-water partition coefficient
LOQ	Limit of quantitation
LUGV	Landesamt für Umwelt, Gesundheit und Verbraucherschutz
LUWG	Landesamt für Umwelt, Wasserwirtschaft, und Gewerbeaufsicht
m/z	Mass to charge ratio
MDL	Method detection limit
MeOH	Methanol
Monoglyme	Ethylene glycol dimethyl ether
MS	Mass spectrometry
MTBE	Methyl *tert*-butyl ether
n.d.	Not detected
NICNAS	National industrial chemicals notification and assessment scheme
OECD	Organization for economic co-operation and development
OPs	Organophosphates
OSPA	Oxygenated solvent producer association
PET	Polyethylene tetraphthalate
P_{oc}	Organic carbon partition coefficient
ppm	Parts per million

R^2	Coefficient of determination
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RIWA	Rhine water works
RSD	Relative standard deviation
RT	Retention time
SD	Standard deviation
SIM	Selected ion monitoring
SPE	Solid phase extraction
SPME	Solid phase microextraction
STP	Sewage treatment plant
SU	Surrogate
SW	Surface water
TBEP	Tris(2-butoxyethyl) phosphate
TCEP	Tris (2-chloroethyl) phosphate
TCPP	Tris (2-chloro-1-methylethl) phosphate
TDCP	Tris(1,3-dichloro-2-propyl) phosphate
Tetraglyme	Tetraethylene glycol dimethyl ether
TiBP	Tri-iso-butyl phosphate
TnBP	Tri-n-butyl phosphate
TOC	Total organic carbon
Triglyme	Triethylene glycol dimethyl ether
U.S. EPA	United States Environmental Protection Agency
v/v	Volume by volume
WDC	Wesel Datteln Canal
WWTP	Wastewater treatment plant
ZALF	Leibniz-Centre for Agricultural Landscape Research

Chapter 1 Introduction

1.1 Target analytes

The focus of many environmental investigations has been placed on organic contaminants such as pharmaceuticals, endocrine disruptors, pesticides, oxygenated gasoline additives, perfluorinated organic compounds, and phenolic compounds (Loos et al., 2009, Kim et al., 2007, Kasprzyk-Hordern et al., 2008, Skutlarek et al., 2006, Konstantinou et al., 2006, Herrero-Hernández et al., 2013). The objective of the present thesis was to study the behavior of hydrophilic ethers in the aquatic environment. For that purpose six not commonly investigated ethers have been selected: ethyl *tert*-butyl ether (ETBE), 1,4-dioxane, ethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme). The chemical structures of the target analytes and of an internal standard (4-chlorotetrahydropyran) are presented in **Figure 1.1**. 1,4-Dioxane is a cyclic diether, whereas the four selected glycol dimethyl ethers contain a varying number of characteristic ethylene glycol units. ETBE has been chosen for the analysis because fuel oxygenates are widely used in Europe and many have a profound effect on the water bodies. Pollution of ground waters with 1,4-dioxane, resulting from its use as solvent stabilizer, has been reported in many countries around the world, however limited number of studies have been conducted in Europe thus far (Mohr, 2010). Although, monoglyme, diglyme, triglyme, and tetraglyme are a group of glycol ethers commonly used in various industries, the data on their possible occurrence in the aquatic environment is scarce.

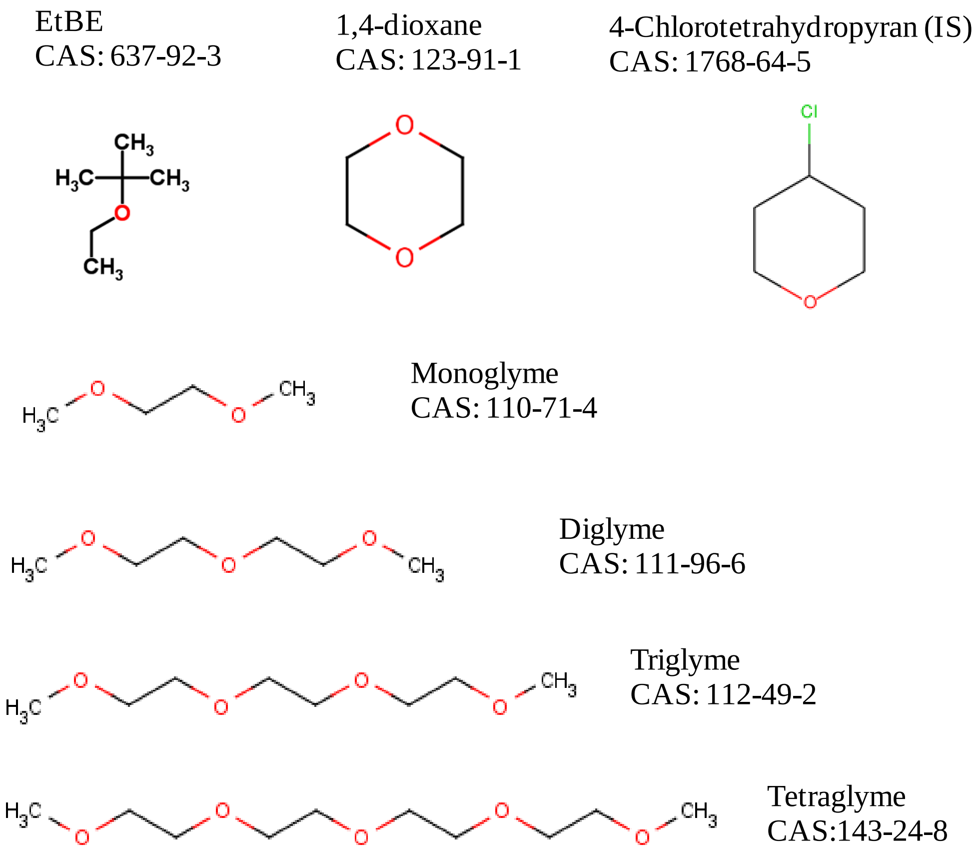


FIGURE 1.1 Chemical structures of target analytes: ETBE, 1,4-dioxane, 4-chlorotetrahydropyran, monoglyme, diglyme, triglyme, and tetraglyme with CAS numbers.

Investigations of the chosen target analytes in the aquatic environment in Europe have not been very common. **Table 1.1** lists a summary of reported concentrations for ETBE, 1,4-dioxane and glymes in European surface-, drinking-, and ground waters. The majority of studies on the oxygenated fuel additives focused on methyl *tert*-butyl ether (MTBE). ETBE has been only sporadically determined in the water systems, although it is widely used in many European countries. Fayolle-Guichard et al. (2012) in the study from Spain, demonstrated the extent of groundwater contamination in the proximity to an oil storage tank, where ETBE concentration reached 301 mg L^{-1}. Moreover groundwater and surface water pollution with ETBE has been reported in Germany, with maximum concentration reaching 2.8 µg L^{-1} and 1.2 µg L^{-1}, respectively (LUBW, 2010; Stupp et al. 2012). Also, high concentrations in the groundwater in Switzerland (11.8 – 13.1 µg L^{-1}) have been determined. Although a concern of the water pollution with 1,4-dioxane has been previously reported in the U.S. and Japan, there has not been a great deal of analysis done on 1,4-dioxane in Europe (Chapter 4). 1,4-Dioxane has been detected in the leachates from municipal landfills and in the industrial wastewater at maximum concentrations of 36 µg L^{-1} and 6,400 µg L^{-1}, respectively (Paxéus, 2000; Romero, 1998). Moreover, an investigation conducted in Denmark in 1990, showed high concentrations of 1,4-dioxane in cosmetic products as well as dish washing liquids, reaching 96 mg/kg (Rastogi, 1990). Even though concentrations of 0.5 µg L^{-1} have been detected in the drinking water in the Netherlands, no further studies in Europe have been conducted and reported (European Commission, 2002). The most recent report on the concentration of 1,4-dioxane in surface waters come from the Rhine River in the Netherlands where in 2012, a maximum concentration reached 1.7 µg L^{-1} (Rhine Water Works, 2012). The same agency also conducts investigations on the current levels of di-, tri-, and tetraglyme in the river Rhine. These glymes have been included in the list of the target substances in response to the high concentrations detected in the Rhine River in 2005. **Figure A.2 b-d** illustrates the detected concentration of diglyme, triglyme, and tetraglyme in the Rhine River, since their monitoring began.

Already the first sampling campaign conducted in Germany (Chapter 2) demonstrated that levels of ETBE in the surface waters are very low. In 2005, ETBE was introduced as a fuel additive in Germany in order to phase out the commonly applied MTBE (Stupp et al, 2008). According to the German Bioethanol Industry Association, 366,000 tons of bioethanol (79.6 %) was used for the production of ETBE in 2005 in Germany. In 2010, the majority of bioethanol was directly mixed with gasoline, and only 125,000 tons (10.8 %) were used for the ETBE production (**Figure A.1**). Hence, it can be concluded that in Gemany ETBE is being replaced by ethanol/bioethanol. Other European countries such as Spain, France, and Italy are the main markets for ETBE consumption; hence greater contamination of water bodies with ETBE is expected. ETBE is continuously analyzed in the Rhine River at the Lobith station, Netherlands by the Rhine Water Works (**Figure A.2a**). Between 2005 and 2010 concentration waves exceeding 5.0 µg L^{-1} were occasionally reported. Currently, concentrations above the detection limit are rarely detected. In the surface water monitoring studies conducted within this thesis, concentrations close or below the detection limit were commonly determined for ETBE. Therefore, it is not further regarded in the subsequent discussion. Nevertheless, it was the first time that a solid phase extraction method was used for the enrichment of ETBE from water samples. Moreover, very good extraction recoveries were achieved (Chapter 2).

TABLE 1.1 Reported concentrations of ETBE, 1,4-dioxane and glymes in the aquatic environment in Europe.

Location	Matrix	Levels observed	References
1,4-dioxane			
Denmark	Cosmetic products Dish washing liquids	0.3 – 96 ppm (mg/kg) 1.8 – 65 ppm (mg/kg)	Rastogi, 1990
1. Netherlands 2. Drente, Netherlands 3. Germany	Drinking water Surface water Surface water (Rhine River)	0.5 µg/L 1 – 10 µg/L < 10 µg/L	European Commission, 2002
United Kingdom	Unspecified river	Not given	Gelman Sciences, 1989c
Göteburg, Sweden	Municipal landfills	8-36 µg/L	Paxéus, 2000
Barcelona, Spain	Industrial waste water from polyester resin producers	6,400 µg/L (<100 – 31,400 µg/L)	Romero, 1998
Netherlands	Surface water	Max. 1.1 µg/L (Lekkanal) Max. 1.7 µg/L (Rhine River)	Rhine Water Works, 2012
ETBE			
Baden-Württemberg, Germany	Groundwater	Max. 2.8 µg/L	LUBW, 2010
Catalonia, Spain	Groundwater	Max. 0.68 µg/L	Rosell et al., 2003
Netherlands	Groundwater Surface water	0.1 – 1.0 µg/L 0.1 – 1.0 µg/L	Van Wezel et al., 2009
France	Contaminated GW close to oil storage tank	301 mg/L	Fayolle-Guichard et al., 2012
1. Morbio Inferiore Switzerland, 2008 2. Canton St. Gallen Switzerland 2000-2009 3. Bavaria, Germany 2006-2010 4. Saxony, Germany 2008-2010 5. Sweden 6. Bavaria, Germany 2006-2008 7. Saxony, Germany 2009	Groundwater Groundwater Groundwater Groundwater Drinking water Surface water (Danube, Main Rivers) Surface water (Elbe, lakes, tributaries)	11.8 – 13.1 µg/L max. 1.021 µg/L max. 0.331 µg/L max. 2.41 µg/L 0.0079 µg/L Max. 0.4 µg/L, Avg. 0.036 µg/L Max. 1.2 µg/L, Avg. 0.88 µg/L	Stupp et al., 2012
Lobith, Netherlands 2005-2013	Surface water (Rhine River)	Figure A.2a	IAWR, 2013

Location	Matrix	Levels observed		References
Glymes				
Netherlands	Surface waters (Rivers Rhine, Meuse, Scheldt, Noordwijkerhout)	0.060-0.900 µg/L Diglyme 0.003 -1.000 µg/L Triglyme 0.200-0.600 µg/L Tetraglyme		van Stee, 2002
Lobith, Netherlands 2005-2013	Surface water (Rhine River)	Diglyme Triglyme Tetraglyme	Figure A.2 b-d	IAWR, 2013

1.2 Toxicity

The concern with many emerging organic contaminants is associated with the toxicological effects to their exposure. The selected ether compounds do not bioaccumulate in the environment; however, they contribute to the negative health effects when in contact with humans. According to U.S. Environmental Protection Agency (U.S. EPA) and the International Agency for Research on Cancer (IARC), 1,4-dioxane is a probable human carcinogen (Group B2) based on the inadequate evidence in humans and sufficient data from laboratory animal studies. Exposure to high levels of 1,4-dioxane may result in severe kidney and liver effects and possibly death (Agency for Toxic Substances and Disease Registry [ATSDR], 2012). Numerous studies on animals have shown that breathing 1,4-dioxane vapors, ingestion of contaminated water and/or skin contact affects mainly nasal cavity, liver and kidneys. Experimental studies on exposure of animals to monoglyme, diglyme, and triglyme showed reproductive and developmental effects as well as genotoxicity (Hardin, 1983; George et al.,1987; Schwetz et al., 1992; European Centre for ecotoxicology and toxicology of chemicals [ECETOC], 2005). Hence, contact with these glymes may cause infertility and harm to the unborn child (U.S. EPA, 2011). Moreover, destruction of the red blood cells and blood forming organs may follow. Most of the toxic effects of glymes arise as a result of the metabolic conversion of the glycol ether into 2-methoxyethoxyacetic acid generated from 2-methoxyethanol (ECETOC, 2005). Supposedly, the presence of longer alkyl groups at the glyme terminal ends and more ethylene glycol groups in the middle of the glyme molecule both act to reduce the toxicity of the ether. Therefore, negative health effects of triglyme and tetraglyme is expected to be lower than for monoglyme and diglyme (ECETOC, 2005).

1.3 Formation of 1,4-dioxane as a by-product

The majority of 1,4-dioxane sources in the aquatic environment are associated with its use as a solvent stabilizer for 1,1,1-trichloroethane (1,1,1-TCE). Many groundwater aquifers have been extensively contaminated through the incorrect handling, storage and disposal practices. Since 1995 the use of 1,1,1-TCE has been regulated by the Montreal Protocol, because of its ozone depleting properties, hence the use of 1,4-dioxane as its stabilizer has subsided. Another major source of 1,4-dioxane is its formation as a by-product during several ethoxylation reactions. Ethoxylation is a chemical process where ethylene oxide is added to fatty alcohols or to fatty acids to produce non-ionic surface active agents (surfactants). Ethoxylated surfactants can be found in household and industrial cleaners, topical pharmaceuticals, cosmetics and laundry detergents as foaming agents, emulsifiers and wetting agents (Mohr, 2010). During the ethoxylation process, ethylene oxide is combined and rearranged to form the polymer of ethylene oxide. In the presence of an acid catalyst, ethylene oxide can dimerize to form 1,4-dioxane **(Figure 1.2)**. The formation of 1,4-dioxane during ethoxylation can be reduced by controlling mixing ratios, temperatures, and other reaction parameters. One of the earliest determination of 1,4-dioxane in ethoxylated surfactants was addressed by Robinson and Ciurczak (1980) and Scalia (1990).

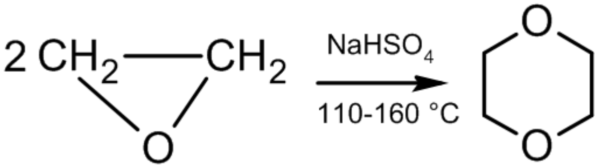


FIGURE 1.2 Dimerization of ethylene oxide to 1,4-dioxane.

As shown in **Figure 1.3**, 1,4-dioxane may form as a by-product during sulfation reaction of alcohol ethoxylates. A common ingredient of cosmetics sodium laureth sulphate is produced through ethoxylation of sodium dodecyl sulphate.

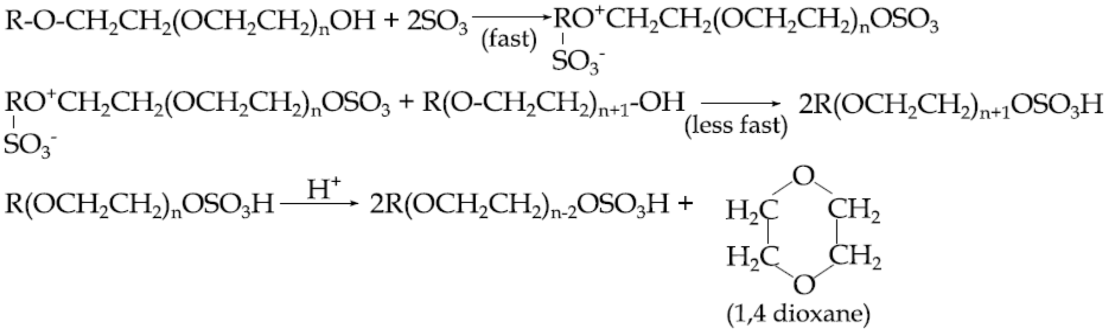


FIGURE 1.3 Sulfonation of ethoxylated alcohols to alcohol ether sulfates. (*Source*: Ortega, 2012)

1,4-Dioxane may also form as a byproduct during esterification reaction in the production of polyethylene terephthalate (PET) (Popoola, 1991). The mechanism of 1,4-dioxane formation during PET production is shown in **Figure 1.4**.

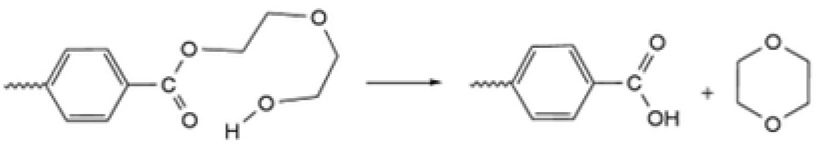


FIGURE 1.4 Formation of 1,4-dioxane during PET production. (*Source*: Schiers and Long, 2003)

Black et al. (2001) investigated the presence of 1,4-dioxane in cosmetics in the USA and reported concentrations of up to 1410 ppm in raw materials and 279 ppm in finished products. Fuh et al. (2005) detected 1,4-dioxane in non-ionic surfactants manufactured in Taiwan, but not in the three cosmetic products obtained from USA and Europe. The maximum concentration in shampoo equaled to 41.1 ppm, 7.8 ppm in a liquid soap sample and 6.5 ppm in a dish washing detergent. In the unpublished study conducted between 2007 and 2010 by the Independent Organic Consumer Association in the USA, 1,4-dioxane was present at a maximum concentration of 24 ppm in shampoos, 29 ppm in laundry detergents and 23 ppm in body wash. Moreover, many personal care products made especially for children contained high concentrations of 1,4-dioxane (up to 12 ppm). Also in Germany, numerous samples of shampoos and body washes (n = 34) were investigated. The average concentration of 1,4-dioxane was found to be between 1 and 2 ppm (Chemische und Veterinäruntersuchungsamt Karlsruhe und Freiburg, 2011). In 1988, the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) set a limit of 10 ppm (mg/kg) for 1,4-dioxane as an impurity in the final cosmetic products (Fruijtier-Pölloth, 2005).

Although the limit was not exceeded in the performed study, the objective is to lower the allowed concentration of 1,4-dioxane in personal care products in Germany. Results of these independent studies show that general public is exposed to 1,4-dioxan on daily basis. Consumers wishing to avoid exposure to 1,4-dioxane are advised to refrain from products containing ingredients or partial ingredient names that include: sodium laureth sulfate, polyethlylene, polyethylene glycol, and ceteareth.

1.4 Focus of the research

The extensive use of the ETBE, 1,4-dioxane, and glymes in the industry and the lack of information about their presence and behavior in the aquatic systems command for more research. In order to gain knowledge about the occurrence, behavior, and fate of ETBE, 1,4-dioxane and glymes in the aquatic environment, several questions were addressed in the present doctoral thesis:

I. **Method development for hydrophilic ethers** – does a suitable method exists for determination of the hydrophilic ethers in various aquatic compartments at concentrations below 100 ng L^{-1} (surface-, drinking-, ground-, wastewater)? Can a method be validated for all the target analytes and matrices?

II. **Behavior of 1,4-dioxane and glymes during bank filtration and in the anoxic aquifer** – Are 1,4-dioxane and glymes attenuated during bank filtration processes? Do they persist in the anoxic aquifer? Are they stable in during the ongoing reduction processes in the groundwater and can they be used as organic tracers?

III. **Distribution of 1,4-Dioxane in the aquatic environments** – What is the spatial and temporal distribution of 1,4-dioxane in major rivers in Poland and Germany? What is the average load of 1,4-dioxane in the surface waters? Is 1,4-dioxane present in the influents and removed during sewage water treatment? Can 1,4-dioxane be detected in the drinking water produced through managed aquifer recharge? Can sources of 1,4-dioxane be identified?

IV. **Occurrence and sources of glymes in the Oder River** – What is the spatial distribution of monoglyme, diglyme, triglyme, and tetraglyme in the Oder River? Can the area of glyme pollution and their sources in the surface water be identified? Why are high concentrations of glymes discharged into the Oder River?

Chapter 2 Simultaneous determination of six hydrophilic ethers at trace levels using coconut charcoal adsorbent and gas chromatography/mass spectrometry

2.1 Abstract

The main objective of the following study was to determine the efficiency of a method that uses coconut charcoal as a solid-phase extraction (SPE) adsorbent in order to simultaneously detect six hydrophilic ether species in water in the low microgram-per-liter range. The applied method was validated for quantification of: ethyl *tert*-butyl ether, 1,4-dioxane, ethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme) and tetraethylene glycol dimethyl ether (tetraglyme). SPE followed by gas chromatography/mass spectrometry of the extracts using the selected ion monitoring mode allowed for establishing low detection limits in the range of 0.007 – 0.018 µg L^{-1} in ultrapure water and 0.004 – 0.020 µg L^{-1} in environmental samples. Examination of the method accuracy and precision resulted in a recovery greater than 86.8 % for each compound with a relative standard deviation of less than 6.6 %. A stability study established a 5 day holding time for the unpreserved water samples and extracts. Finally, 27 samples obtained from surface water bodies in Germany were analyzed for the six hydrophilic ethers. Each analyte was detected in at least eight samples at concentrations reaching 2.0 µg L^{-1}. The results of this study emphasize the advantage of the method to simultaneously determine six hydrophilic ether compounds. The outcome of the surface water analyses augments a concern about their frequent and significant presence in surface water bodies in Germany.

2.2 Introduction

The number of chemical compounds previously not detected or discovered in the water is growing. Many of them pose a risk to humans and the environment but only some are considered “contaminants of emerging concern” (U.S. Environmental Protection Agency, 2010). The presence, frequency of occurrence, and sources of ethyl *tert*-butyl ether (ETBE), 1,4-dioxane, ethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) in surface waters are not well established. The International Agency for Research on Cancer listed 1,4-dioxane as a possible carcinogen to humans (Group B2), and toxicology studies revealed that glymes are toxic to the reproductive and/or developmental systems causing infertility and harm to the unborn children (U.S. Environmental Protection Agency, 2011). In 2011, the U.S. Environmental Protection Agency regulated 14 glymes, including the four glymes being subject of the present study, in order to limit the manufacture, import and processing of these toxic chemicals in the USA. The European Union restricts the use of monoglyme, diglyme, and triglyme to professional users (Directive 2003/36/EC) and limits their use in the manufacture of cosmetics (Directive 76/768/EEC) and toys (Directive 2009/48/EC).

The selected target compounds have been previously analyzed in the aquatic environments using various methods. 1,4-dioxane has been detected in waste-, surface, and ground waters as well as drinking waters, using extraction techniques such as purge and trap, liquid-liquid extraction, solid-phase microextraction (SPME), and solid-phase extraction (SPE) followed by both, gas chromatography (GC) and gas chromatography–mass spectrometry (GC/MS) (Zenker et al., 2003; Park et al., 2005; Shirey and Linton, 2006). ETBE is usually determined in water using techniques, such as purge and trap, direct aqueous injection, headspace, and SPME (Inal et al,, 2006). To the best of our knowledge, ETBE has not been determined by SPE thus far. Glymes have rarely been a focus of environmental analysis. Xu-Liang Cao et al. (2001) monitored glymes in a fuel exhaust using graphitized carbon black and GC/MS (Cao and Zhu, 2001). Benson et al. (1999) analyzed mono-, di-, and triglyme by solid-phase micro-extraction and GC/flame ionization detector. Di-, tri-, and tetraglyme were detected in a wide-range screening study of micro-contaminants in surface water that used XAD-4 and XAD-8 for extraction and GC-atomic emission detector/MS for the detection (van Steel et al., 2002). This is the first study that focuses on the method validation for the four glyme compounds in surface water samples by use of only one analytical procedure.

The analytes chosen for this study are utilized in numerous industrial sectors. 1,4-dioxane is mainly used as a processing solvent in the production of adhesives, paint strippers, dyes, degreasers, fabric cleaners, paper, electronics, and many more (Sei et al, 2010). It is also formed as an undesired by-product in industrial processes, such as synthesis of polyester and ethoxylation (Sei et al., 2010, Black et al., 2001). ETBE is a fuel oxygenate used in numerous countries as an antiknock agent and to enhance fuel combustion. Glycol dimethyl ethers (glymes) are saturated polyethers, commonly used as reaction solvents in the area of pharmaceutical or specialty chemical production. They also find widespread use in the manufacturing of numerous products including printing inks, paints and coatings, adhesives, batteries, and break fluids (U.S. Environmental Protection Agency, 2011).

According to the European Chemical Substances Information System, the production of 1,4-dioxane, ETBE and diglyme exceeds 1,000 t/year in at least one member country placing them on the list of high production volume chemicals. As reported in the European Union Risk Assessment Report in 2002, the production of 1,4-dioxane in Europe is limited to only one production site. In 1997, BASF AG in Ludwigshafen, Germany reported a production volume of 2,000-2,500 t (European Commission, 2002). Production of ETBE in Germany was initiated in 2005 in order to phase out methyl *tert*-butyl ether. Although the manufacture of ETBE from bioethanol reached 367,000 tons in 2008, it decreased down to 125,000 tons in 2010 (German Bioethanol Industry Association, 2011). The Organization for Economic Co-operation and Development (OECD) registered monoglyme as a high production volume chemical since it is produced in at least one OECD member state was at 1,000 tons/year (European Chemicals Agency, 2011b). The European production of triglyme exceeded 1,000 tons in 2002 according to the Oxygenated Solvent Producer Association (European Chemicals Agency, 2011b). The production of tetraglyme has not been reported by the European Union industries (as of the time the article was printed).

Table 2.1 lists the CAS numbers, molecular weights (in grams per mol) and selected physicochemical properties relevant to environmental behavior of the ETBE, 1,4-dioxane and four glymes. Ether compounds considered in this study are moderate to highly miscible in water and have Henry's law constants ranging from 1.04×10^{-14} to 1.64×10^{-3} atm $\times$ m^3 $\times$ mol^{-1}

(tetraglyme and ETBE, respectively), ensuring low volatility from aqueous solutions. Based on their *n*-octanol-water partition coefficient (log P_{ow} = −1.03 to 1.92), they exert negligible potential for bioaccumulation. Their high vapor pressures (< 0.01 to 124 mm Hg) ensure fast volatilization from dry soils. Therefore, the main target compartment of ETBE, 1,4-dioxane, and glymes is presumed to be the hydrosphere. Their physicochemical properties imply their difficult removal from water and wastewater, which greatly increases the potential for surface and groundwater contamination.

TABLE 2. 1 CAS numbers, molecular weight, and relevant physiochemical properties of ETBE, monoglyme, 1,4-dioxane, diglyme, triglyme, and tetraglyme.

Analyte	CAS No.	Molecular weight (g/ mol)	Water solubility (at 25°C; g/L)	Vapor pressure (mm Hg at 25°C)	Henry´s law constant (atm× m^3× mol^{-1})	Log P_{ow} (at 25 °C)
EtBe	637-92-3	102.18	13.6	124	1.64×10^{-3}	1.92
Monoglyme	110-71-4	90.12	85.2	79.2	1.07×10^{-6}	-0.21
1,4-dioxane	123-91-1	88.11	101.5	38.1	4.88×10^{-6}	-0.27
Diglyme	111-96-6	134.18	162.0	3.01	5.23×10^{-7}	-0.36
Triglyme	112-49-2	178.23	208.8	0.24	4.88×10^{-12}	-0.76
Tetraglyme	143-24-8	222.28	263.9	<0.01	1.04×10^{-14}	-1.03

[a] U.S. EPA (2011b). Estimation Program Interface Suite™ for Microsoft® Windows, v 4.10. US Environmental Protection Agency, Washington, DC, USA [7].

P_{OW} – *n*-Octanol/Water Partition Coefficient

The objective of this paper was to determine a method and conduct an experimental and analytical validation in order to allow for simultaneous detection of six hydrophilic ethers in environmental samples.

2.3 Experimental

2.3.1 Chemical standards and reagents

ETBE (97 %) and tetraglyme (98 %) were purchased from Fluka (Steinheim, Germany). Monoglyme (99 %), 1,4-dioxane-d_8 (99 %), and 4-chlorotetrahydropyran (96 %) were obtained from Sigma-Aldrich (Steinheim, Germany). 4-Chlorotetrahydropyran was used as an internal standard (IS) and 1,4-dioxane-d_8 as a surrogate (SU). Diglyme (99 %) and 1,4-dioxane (99.5 %) were supplied by Dr. Ehrenstorfer (Ausgburg, Germany) and Ultra Scientific (Kingstown, USA), respectively. Triglyme (99.8 %) was purchased from Alfa Aesar (Karlsruhe, Germany). Analytical grade dichloromethane (DCM), distilled before use and hypergrade methanol were both obtained from Merck (Darmstadt, Germany). Astacus ultrapure water purification system, from MembraPure (Bodenheim, Germany), was used to produce ultrapure water. A stock solution of the analytes was prepared in methanol at concentration of 1 µg µL^{-1}. The IS and surrogate stock solutions used were prepared in methanol, each at 1 µg µL^{-1} concentration. Working standard solutions and calibration curves were prepared using appropriate dilutions of stock solutions in methanol or dichloromethane.

2.3.2 Sample collection

Surface water samples were collected from seven water bodies located in Germany, where significant concentrations of the analytes of interest were previously reported or suspected. **Table 2.2** lists locations of river samplings in Germany together with grid values of sampling sites and sampling dates. Two sampling campaigns were done in the month of October, resulting in a total of 23 samples. The Oder River sampling was carried out in February, adding four additional samples into the study. The river samples were collected without preservation in 500 mL or 1 L amber glass bottles. Containers were cleaned before use with distilled water and acetone followed by heating in the oven at 110 ºC for at least 2 h. The surface water samples were collected along the shore line of the river bodies. Each bottle was filled leaving no headspace and stored in the refrigerated storage room at 6 ºC for a maximum of 2 days. Surface water samples were not filtered prior to the extraction, only decanted if necessary. The extracts were analyzed immediately after the extraction.

TABLE 2.2 Locations of river samplings in Germany, grid values of sampling sites and sampling dates.

Sample ID	River	Location	Grid Values		Sampling date
SW1	WDC	Marl	51°40' 9.8034" N	7° 6' 52.2648"E	08 Oct 2011
SW2	WDC	Dorsten	51°39' 53.3622" N	6° 57' 59.4426"E	08 Oct 2011
SW3	WDC	Huenxe	51° 38' 56.4072" N	6° 47' 8.7102"E	08 Oct 2011
SW4	WDC	Wesel	51° 38' 6.4320" N	6° 39' 33.3756"E	08 Oct 2011
SW5	Lippe	Dorsten	51° 40' 5.6526" N	6° 57' 39.0492"E	08 Oct 2011
SW6	Rhein	Wesel	51° 39' 25.7142" N	6° 35' 43.9116"E	08 Oct 2011
SW7	Rhein	Voerde	51° 36' 9.2592" N	6° 35' 51.7878"E	08 Oct 2011
SW8	Rhein	Voerde	51° 34' 44.7450" N	6° 40' 0.0042"E	08 Oct 2011
SW9	Rhein	Duisburg	51° 25' 51.5136" N	6° 43' 9.0120"E	09 Oct 2011
SW10	Rhein	Leverkusen	51° 1' 56.9352" N	6° 57' 59.0184"E	09 Oct 2011
SW11	Rhein	Koeln	50° 58' 38.4918" N	6° 59' 57.0150"E	09 Oct 2011
SW12	Rhein	Bad Honnef	50° 39' 21.8592" N	7° 12' 28.0146"E	09 Oct 2011
SW13	Rhein	Wiesbaden	50°1' 40.4904" N	8° 15' 22.4712"E	09 Oct 2011
SW14	Rhein	Wiesbaden	50°1' 58.9296" N	8° 14' 39.9264"E	09 Oct 2011
SW15	Rhein	Wiesbaden	50°1' 58.9296" N	8° 14' 39.9264"E	09 Oct 2011
SW16	Main	Hanau	50°7' 35.3892" N	8° 52' 20.3664"E	22 Oct 2011
SW17	Main	Frankfurt	50°7' 55.5708" N	8° 46' 7.3158"E	22 Oct 2011
SW18	Main	Offenbach	50°6' 37.0542" N	8° 44' 7.8714"E	22 Oct 2011
SW19	Main	Kelsterbach	50°4' 12.8454" N	8° 31' 37.1532"E	23 Oct 2011
SW20	Main	Kelsterbach	50°3' 17.6544" N	8° 30' 40.5966"E	23 Oct 2011
SW21	Main	Ruesselsheim	49°59' 58.0446" N	8° 24' 57.2508"E	23 Oct 2011
SW22	Schwarzbach	Trebur	49°55' 20.6544" N	8° 24' 44.4450"E	23 Oct 2011
SW23	Rur	Düren	50°30'6.972" N	6° 26' 37.4598"E	24 Oct 2011
SW24	Oder	Genschmar	52°37'54.5268" N	14° 32' 19.2798"E	01 Feb 2012
SW25	Oder	Groß- Neuendorf	52° 37'1.3176" N	14° 24' 51.8610"E	01 Feb 2012
SW26	Oder	Güstebieser Loose	52° 45'41.3598" N	14° 19' 4.2450"E	01 Feb 2012
SW27	Oder	Bienenwerder	52° 48'44.4954" N	14° 13' 19.7214"E	01 Feb 2012

WDC Wesel Datteln Canal

2.3.3 Extraction procedure

The analytes were extracted and enriched from water using "Resprep® activated coconut charcoal SPE cartridges" (Restek, 80-120 mesh, approximately 150 µm, 2g, 6 mL). The extraction procedure has been adopted from the EPA 522 method, developed by Environmental Protection Agency for the determination of 1,4-dioxane in drinking water samples (U.S. Environmental Protection Agency, 2008). Cartridge processing station VacElut 20 (Varian, Germany) was used to mount a maximum of 20 cartridges. In order to remove impurities, the cartridges were conditioned with 3 mL of DCM, followed by 3 mL of methanol, aspirating completely using a vacuum set at 850 mbar. From then on, the cartridges were not allowed to dry, leaving a solvent just above the top frit. An additional 3 mL of methanol were added to the cartridge followed by 12 mL of ultrapure water to prepare the material for sample loading. Five hundred milliliters of the water sample was loaded onto the cartridge containing 2 grams of adsorbing material. Prior to the extraction each sample, blank and control standard were enriched with 5 µL of surrogate (1,4-dioxane-d_8, 1 µg/µL). Cartridges and teflon tubes, filled with ultrapure water, were connected via Teflon adapters. Samples were allowed to percolate through the absorbing material at a vacuum of 850-900 mbar. To minimize the contact of the samples with ambient air in the laboratory, the openings of the bottles where covered with Parafilm (Pechiney Plastic Packaging, Chicago, IL). After the sample passed through, the cartridges were dried at 680 mbar for 10 minutes. The analytes were eluted at low vacuum with dichloromethane until the 9 mL mark on the collection tubes was reached. Subsequently, the extracts were adjusted to a final volume of 10 mL with dichloromethane. These steps lead to an enrichment of the analytes by a factor of 50 taking into account that always 500 mL of water sample was used for an extraction. The DCM layer was transferred to a 10 mL vial for storage and 500 µL of the sample extract with 10 µL of an IS (0.125 µg/µL , 4-chlorotetrahydropyran) were placed in the autosampler vial for GC/MS analysis.

2.3.4 GC/MS analytical conditions

Trace GC system coupled to a Voyager MS instrument (ThermoQuest Finnigan, Dreieich, Germany) was used to identify and quantify ETBE, 1,4-dioxane, 1,4-dioxane-d_8, 4-chlorotetrahydropyran, monoglyme, diglyme, triglyme, and tetraglyme. The GC was equipped with either a CS-624 (CS Chromatographie Service Gmbh, Langerwehe, Germany) or DB-624

(Agilent, Waldbronn, Germany) column with the dimensions of 30 m length × 0.25 mm ID and 1.40 µm film thicknesses. Two µL of each extract was injected using Combi PAL autosampler (CTC Analytics, Switzerland). The injector was operated at 240 ºC in a splitless mode of 1 min and a split flow of 50 mL/min. The initial oven temperature of 37 ºC was kept for 2.5 minutes, ramped to 75 ºC at 4 ºC/min, with a final increase to 220 ºC at a 10 ºC/min. During the recovery and precision studies, the last ramping was changed to 20 ºC/min, resulting in a shorter run without separation problems. Helium (≥99.999%) was used as a carrier gas at a constant flow of 1 mL/min. The mass spectrometer was operated in electron impact mode with electron energy of 70 eV. The source temperature and GC interface temperature were kept at 220 °C and 250 °C, respectively. The emission current was 150 µA and the detector voltage was set at 500 V. XCalibur software (Thermo Fisher Scientific, version 2.0.7) was used to process all of the acquired data.

2.3.5 Quantification and quality control

In order to quantify the analytes at low parts per billion (in micrograms per liter) levels, the standards and samples were acquired in the selected ion monitoring (SIM) mode. Initially, the standards were scanned from *m/z* 45–250 to determine the retention times and to select the ions for identification and quantification of the compounds studied. Example of a chromatogram with a standard run in TIC and SIM mode is presented in **Figure A.3**. In the samples, the analytes were identified by comparing their selected ions and retention time to the daily calibration or calibration verification standards. The calibration curves, standards and samples were acquired with time scheduled SIM mode presented in **Table 2.3**.

TABLE 2.3 GC/MS in time scheduled selected ion monitoring (SIM) acquisition program (example): retention time window (minutes), retention time (RT), dwell time, target (*T*) and confirmation (*Q*) ions as well as abundance ratio.

				Selected Ions			Abundance Ratio	
Analyte	**RT window**	**RT (min)**	**Dwell time**	T	Q_1	Q_2	Q_1/T	Q_2/T
ETBE	6.30-7.20	6.85	0.2	59	87	88	0.48	0.21
Monoglyme	7.20-9.50	8.63	0.133	45	60	90	0.16	0.14
1,4-dioxane--d8 (SU)	9.50-16.30	10.58	0.1	96	64	62	0.35	0.23
1,4-dioxane	9.50-16.30	10.7	0.1	88	58	87	0.36	0.14
IS	16.30-18.00	17.48	0.2	55	54	120	0.36	0.2
Diglyme	18.00-21.00	18.33	0.133	59	58	89	0.51	0.42
Triglyme	21.00-36.0	23.49	0.133	59	58	103	0.46	0.43
Tetraglyme	21.00-36.0	27.56	0.133	59	58	103	0.44	0.50

With the aim of confirming the presence of a compound in each sample, the abundance of the confirmation ions relative to the target ion had to agree within an absolute 20 % of the relative abundance in the spectrum taken from the most recent calibration standard analyzed in the SIM mode. An initial calibration consisting of 7–9 points ranging from 2 µg L^{-1} to 1000 µg L^{-1} (corresponding to 0.040 µg L^{-1} to 20 µg L^{-1} in a water sample) was prepared for each analyte. Fixed amounts of IS and SU were added to each calibration level resulting in concentrations of 250 µg L^{-1} and 500 µg L^{-1}, respectively. For each analyte, a calibration curve was created using an IS technique in the Quan Browser of XCalibur software. The calibration curve for each analyte was fitted with a linear regression. The coefficient of determination (R^2) for the linear fit of the calibration curve was ≥ 0.99 for all analytes. The average response factors from the initial calibration were used to calculate the concentration of each compound in the sample. During each day of the analysis, calibration verification standards were run at the beginning and at the end of ten sample batch. Two levels were chosen, one close to the quantitation limit and at the mid-range of the calibration curve. Solvent blanks were run multiply times during the analysis in order to confirm that the solvent and the system are free from interferences. Each extraction batch consisted of maximum 18 samples. Additionally, one method blank and one standard containing all of the analytes of interest and a surrogate were treated in the same way as the samples. The percent of spike and surrogate recovery were monitored to verify the extraction efficiency with an acceptable range of 70–130%.

2.4 Results and discussion

2.4.1 Optimization of the extraction method

During the SPE procedure, major sources of contamination come from reagents and solid-phase extraction devices. It has previously been reported that contaminants may arise from solid phase sorbents and the polypropylene cartridges (Junk et al., 1988). Therefore, potential interferences originating from commercial cartridges had to be investigated. The above described extraction method was applied to three cartridges: Enviro-Clean 521 (UCT, Bristol, PA), method-specific SPE cartridges from Restek (Bellefonte, PA) and Supelclean^{TM} coconut charcoal (Supelco, Taufkirchen, Germany). "Resprep$^{®}$ activated coconut charcoal" SPE cartridges from Restek, developed specifically for EPA methods 521 and 522, proved to have the lowest background and produced no interference with the analytes. For the conditioning of the cartridges, various grades of methanol, acetone and acetonitrile were tested. Although acetone and acetonitrile were applicable, high purity methanol (Merck, Darmstadt) was chosen for the extraction as it created the lowest interference with the early eluting analytes. Lower purity grades of methanol contained compounds with interfering ions, prohibiting identification of the analytes of interest. Possible interferences coming from the extraction were examined by analyzing a method blank with each extraction batch. During this study, all of the method blanks evaluated using the ultrapure water, were below the method detection limits (MDLs) for the target compounds. In an attempt to eliminate residual water from the elution step, the cartridges were dried with nitrogen gas; this step removed the water from the cartridge and the eluent, but resulted in no recovery of the glymes. When the cartridges were completely dried, not only the water, but possibly also the analytes were removed from the adsorbing material.

2.4.2 Precision and accuracy study

The method's accuracy and precision is described in terms of percent recovery and the percent of relative standard deviation (% RSD). To examine the accuracy of the SPE followed by GC/MS-SIM analysis for the six hydrophilic ethers, 500 mL of ultrapure water was enriched with a known amount of investigated analytes. Two concentrations were selected to validate the method: 1 µg L^{-1} and 10 µg L^{-1}. Five microliters of a surrogate (1.0 µg $µL^{-1}$) was added to each sample prior to the extraction and 10 µL of an IS (0.125 µg $µL^{-1}$) was added to each extract. In total, nine spiked water samples were analyzed on two occasions. Linear calibration range was established for each analyte with a $R^2 \geq 0.990$. The calibration verification standards did not exceed the acceptable range of ± 20 %. The results of the study are depicted in the table below (**Table 2.4**).

TABLE 2.4 Precision and accuracy of the method analytes fortified at 1.0 µg L^{-1} and 10.0 µg L^{-1} in ultrapure water.

	Fortified concentration 1.0 µg L^{-1} *(n = 5)*		**Fortified concentration 10.0 µg L^{-1} *(n = 4)***	
Analyte	**Mean % Recovery**	**RSD (%)**	**Mean % Recovery**	**RSD (%)**
ETBE	92.1	5.7	97.5	2.1
Monoglyme	86.8	6.0	108.8	2.5
1,4-dioxane-d_8 (SU)	99.6	6.6	114.1	4.6
1,4-dioxane	97.1	4.1	94.3	3.4
Diglyme	98.2	4.2	112.2	1.3
Triglyme	89.0	3.9	107	2.4
Tetraglyme	89.9	2.0	90.6	1.3

Good recoveries and precisions were obtained at both concentrations. Five ultrapure water samples spiked at 1.0 µg L^{-1} showed recovery range from 86.8 % to 98.2 % for the investigated analytes. The range of recoveries for the four ultrapure water samples fortified at 10.0 µg L^{-1} extended from 90.6 % to 112.2 %. The relative standard deviation (RSD) for all replicate analyses was less than 6.6 % for each compound. During the study, the analytes showed higher recoveries in the extracts fortified at higher concentration. This can be explained by considering the average percent recovery of the surrogate in the samples spiked at 10.0 µg L^{-1} is over 14 % higher than for the 1.0 µg L^{-1} samples. Additionally, during the elution step the top layer of water can prevent from accurately reading the volume of the solvent, resulting in the slightly higher recoveries. It is also probable that the analytes fortified at higher concentrations recover better using the above extraction procedure (Kawata et al., 2001).

2.4.3 Detection and quantification limits

In order to determine a detection limit (MDL) for each analyte statistical approach was used (U.S. Environmental Protection Agency, 2011a). Initially, a 7–point calibration curve that represents concentrations from 0.040 µg L^{-1} to 5.0 µg L^{-1} in the analyzed water samples was prepared for each compound. The average response factors were calculated based on the linear calibration curves with R^2 always greater than 0.990. The procedure for MDL determination in ultrapure water involved fortification and extraction of ten replicates of 500 mL sample at 0.040 µg L^{-1} for 1,4-dioxane, ETBE, diglyme and 0.100 µg L^{-1} for triglyme and tetraglyme. Additionally, eight Main River water samples were spiked with each compound, resulting in a final concentration of 0.040 µg L^{-1}. These concentrations were chosen appropriate based on the analytical and experimental procedure applied. The method blank was analyzed to verify that the extraction is free of contamination that would prevent the identification and exact quantitation of the analytes. The MDL was then calculated as MDL= $t_{(n-1,\ 1-\alpha = 0.99)} \times$ SD where t is the Student’s value appropriate for a 99 % confidence level (t = 2.998) and SD is the standard deviation of the eight replicate analyses (U.S. Environmental Protection Agency, 2008). MDLs and limits of quantification (LOQ) for ETBE, 1,4-dioxane and glymes are shown in **Table 2.5**.

TABLE 2.5 Method detection limit (MDL) and limit of quantiation (LOQ) in micrograms per liter for ultrapure water samples and environmental samples (Main River), together with calibration range and coefficient of determination (R^2) for ETBE, 1,4-dioxane, and glymes.

Analyte	**Calibration Range (µg L^{-1})**	**Ultrapure water *(n = 8)***			**Main River *(n = 8)***		
		R^2	**MDL (µg L^{-1})**	**LOQ (µg L^{-1})**	**R^2**	**MDL (µg L^{-1})**	**LOQ (µg L^{-1})**
ETBE	0.040 - 5.00	0.994	0.013	0.044	0.999	0.020	0.067
Monoglyme	0.040 - 5.00	0.998	0.007	0.024	0.999	0.010	0.032
1,4-dioxane	0.040 - 5.00	0.996	0.010	0.034	0.999	0.016	0.052
Diglyme	0.040 - 5.00	0.998	0.013	0.047	0.998	0.010	0.032
Triglyme	0.040 - 5.00	0.994	0.016	0.055	0.997	0.010	0.035
Tetraglyme	0.040 - 5.00	0.992	0.018	0.057	0.994	0.012	0.041

The following detection limits were established in ultrapure water: 0.013 µg L^{-1} for ETBE, 0.007 µg L^{-1} for monoglyme, 0.010 µg L^{-1} for 1,4-dioxane, 0.011 µg L^{-1} for diglyme, 0.016 µg L^{-1} for triglyme, and 0.018 µg L^{-1} for tetraglyme. The limits of quantitation (LOQ) were calculated by multiplying the average standard deviation of the replicate analysis by 10 (LOQ = SD × 10), and ranged from 0.024 µg L^{-1} to 0.059 µg L^{-1}. The variation as determined from the relative standard deviation for all of the analytes was ≤ 15%. Signal-to-noise ratio for each compound was calculated dividing average concentration of replicates by standard deviation and ranged from 5 to 11. In the environmental samples (Main River), detection limits were: 0.020 µg L^{-1} for ETBE, 0.010 µg L^{-1} for monoglyme, 0.016 µg L^{-1} for 1,4-dioxane, 0.010 µg L^{-1} for diglyme, 0.010 µg L^{-1} for triglyme, and 0.012 µg L^{-1} for tetraglyme. Limit of quantitation spanned from 0.032 – 0.067 µg L^{-1} and the relative standard deviation was below 15.8 %. Signal-to-noise ratio for each analyte was between 9 and 15.

2.4.4 Stability study

To determine the stability of the selected ethers in the water, 20 unpreserved ultrapure water samples and 8 Main River samples were fortified with 5 µL of both a 0.1 µg μL^{-1} standard and 1 µg μL^{-1} surrogate, resulting in a final concentration of 1.0 µg L^{-1} and 10.0 µg L^{-1}, respectively. After spiking, each 500 mL amber bottle was filled to the top, leaving no headspace. The bottles were stored in the dark in the refrigerated storage room at 6 ºC in the time span between spiking and analysis. Extractions with dichloromethane were performed on the day of fortification as well as on the second, fifth and ninth day following spiking. Each time, five ultrapure water samples and two Main River samples were extracted. The concentrations of analytes present in the environmental samples were subtracted from spiked samples. The fortified Main River samples did not contain any materials that adversely affected method performance. The outcome of the stability study for the water samples is shown in the figure below (**Figure 2.1**).

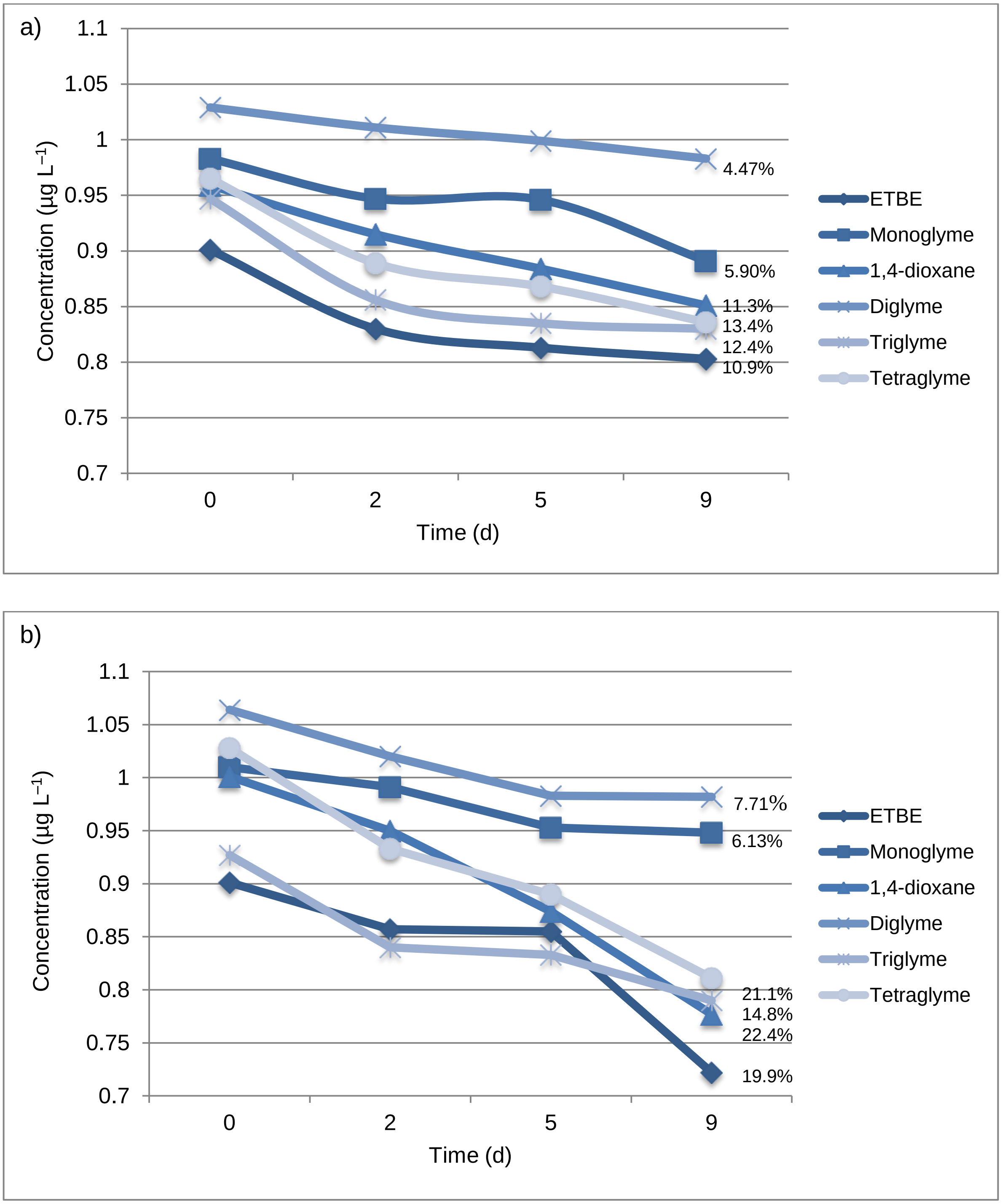


FIGURE 2.1 Stability of ethers in a) ultrapure water (*n* = 5) and b) Main River samples (*n* = 2) with percent difference in the concentration between days 0 and 9.

To establish the stability of the analytes in the dichloromethane, all of the extracts were re-analyzed after 2, 5, 9, and 13 days following the extraction. **Figure 2.2** shows the stability of the extracts during the study. Based on the obtained data, the holding time for both the samples and extracts was established to be 5 days. As shown in **Figure 2.1a** and **2.1b**, ETBE concentration was slightly falling throughout the period of 9 days. This can be explained by its higher vapor pressure and higher Henry's law constant compared with the other ethers. In the ultrapure water concentration of glymes fell between 5.9 % for monoglyme and 13.4 % for tetraglyme. The decrease in the concentrations was more apparent in the Main River samples. Monoglyme concentration fell by 6.13 % and tetraglyme by 21.1 % within the 9 day period. Triglyme and tetraglyme were expected to be more stable in the water samples due to their physicochemical properties, but biodegradation cannot be excluded. 1,4-dioxane concentrations fell by 11.3 and 22.4 % in the ultrapure water and river sample, respectively. The stability of each compound in this particular study resulted in the determination of the sample holding time.

The concentrations in the extracts showed a similar trend (**Figure 2.2**); therefore the extract holding time was also established to be 5 days. All of the samples in this study have been extracted within 2 days of sampling and the extracts were analyzed within 3 days of extraction.

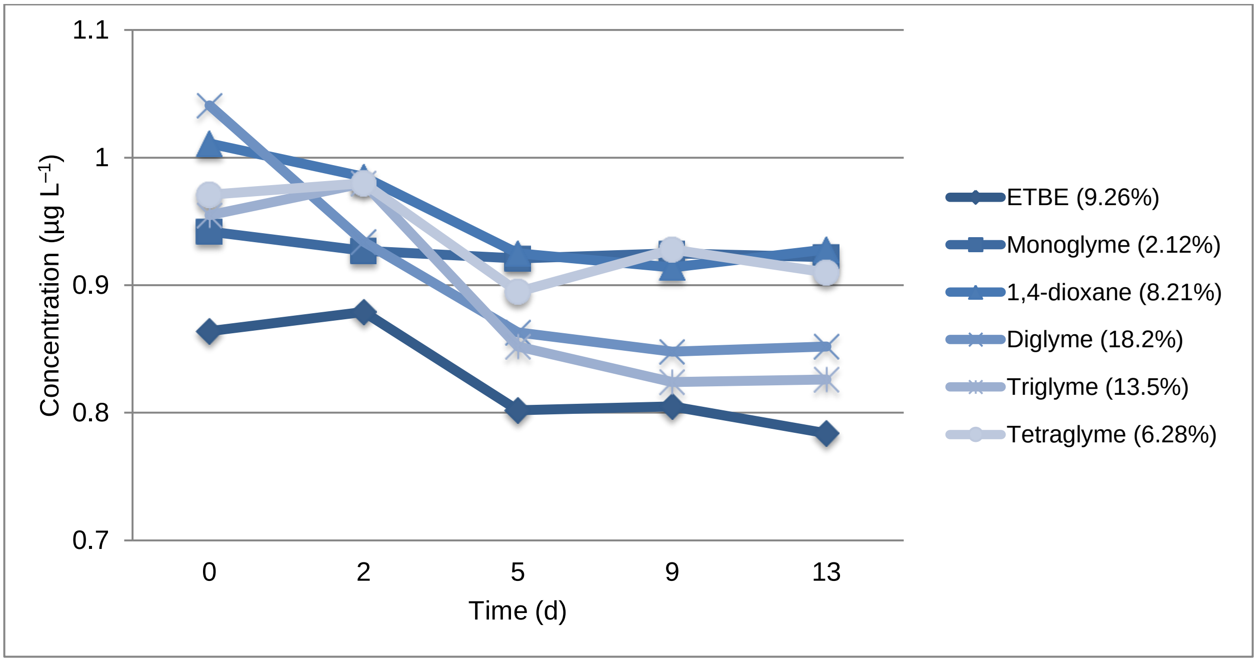


FIGURE 2.2 Stability of ethers in dichloromethane extracts over 13-day period (*n* = *7*). In parenthesis, percent differences in the concentration between days 0 and 13 are shown for each compound.

2.4.5 Application to environmental water samples

To assess the applicability of the above extraction and analytical method, 27 surface water samples were analyzed. Target compounds were unequivocally identified by matching retention times and abundance of the confirmation ions relative to the target ions. Results of the study are reported in the **Table 2.6**. 1,4-dioxane was detected in all of the samples at concentrations that varied between 0.047 µg L^{-1} and 1.92 µg L^{-1}. The highest concentration (1.92 µg L^{-1}) was reported in the Rhine River at the SW8 sampling location (**Table 2.2**). In the Main River the highest concentration of 1.12 µg L^{-1} for 1,4-dioxane was present at the SW21. 1,4-Dioxane was also found in the Lippe, Schwarzbach, Rur, and the Oder River samples with concentrations ranging from 0.20 µg L^{-1} to 1.28 µg L^{-1}. Glymes were detected in numerous samples from the Main, Oder, and Rhine Rivers. Tetraglyme was present with the highest concentration in the Oder River at 1.73 µg L^{-1} (SW27). Monoglyme and diglyme were observed in all of the Rhine River samples with concentrations below 0.427 µg L^{-1} (SW13) and 0.200 µg L^{-1} (SW13), respectively. Diglyme was also detected in the Oder River samples with the average concentration of 0.065 µg L^{-1}. Triglyme was determined in both Oder and Rhine River with the maximum concentration of 0.540 µg L^{-1}(SW25). ETBE was present only in the Wesel Datteln Canal and the Rhine River with the maximum concentration of 0.065 µg L^{-1} (SW14).

Historical and current concentrations of ETBE, diglyme, triglyme and tetraglyme in the Rhine River are available in the database provided by the International Association of Water works in the Rhine (IAWR). The measuring stations are located in Lobith (the Netherlands) and Bimmen (Germany). At these locations, ETBE is analyzed using a purge and trap system combined with GC/MS. A peak concentration reaching 60 µg L^{-1} was recorded for ETBE in October of 2006. The concentrations have decreased over the years. Currently, sporadic high values are detected in the Rhine River; with the majority of the detections being below 0.1 µg L^{-1}. Low levels of ETBE in the German rivers can be explained by the downward trend of production and usage of ETBE. During this study, ETBE was detected in the Rhine River at an average concentration of 0.051 µg L^{-1}. This value agrees with the most recent concentrations recorded. Diglyme, triglyme, and tetraglyme are being analyzed by SPE and GC/MS (exact method unknown) (Rhine Water Works, 2011). Since 2005, glymes have been monitored in the Rhine River in response to the high values observed (Landesamt für Umwelt, Wasserwirtschaft, und Gewerbeaufsicht Rheinland-Pflaz, 2006).

TABLE 2.6 Average, minimum, and maximum (in parenthesis) concentrations of ether compounds (in micrograms per liter) in the surface water bodies in Germany. WDC stands for Wesel-Datteln Canal.

Analyte	**Rhine** *n = 10*	**Lippe** *n = 1*	**WDC** *n = 4*	**Main** *n = 6*	**Schwarzbach** *n = 1*	**Oder** *n = 4*	**Rur** *n = 1*
ETBE	0.051 (0.040-0.065)	n.d.	0.057 (0.044-0.070)	n.d.	n.d.	n.d.	n.d.
Monoglyme	0.275 (0.113-0.427)	n.d.	n.d.	0.114	n.d.	n.d.	n.d.
1,4-dioxane	0.97 (0.364-1.92)	0.672	0.067 (0.047-0.093)	0.506 (0.226-1.12)	0.200	0.816 (0.782-0.891)	1.28
Diglyme	0.119 (0.067-0.200)	n.d.	n.d.	n.d.	n.d.	0.065 (0.050-0.075)	n.d.
Triglyme	0.110 (0.090-0.137)	n.d.	n.d.	n.d.	n.d.	0.492 (0.462-0.540)	n.d.
Tetraglyme	0.086 (0.074-0.097)	n.d.	n.d.	0.409 (0.220-1.25)	n.d.	1.61 (1.47-1.73)	0.192

n.d. not detected

The highest concentration of diglyme detected reached 13 μg L^{-1} in 2006. In the same year, both triglyme and tetraglyme were detected at concentrations as high as 5.11 μg L^{-1} and 2.50 μg L^{-1}, respectively. The concentrations of glymes in the Rhine River have been steadily decreasing since 2006. Since 2009 concentrations of 1 μg L^{-1} and below have been reported.

2.5 Conclusions

Results obtained during this study demonstrate that the proposed analytical method based on SPE as an analyte isolation technique in combination with GC/MS–SIM gives good recoveries and reproducibility for ETBE, 1,4-dioxane, monoglyme, diglyme, triglyme, and tetraglyme in the water samples. Moreover, good performance of the method in terms of detection limit, accuracy, and precision has been demonstrated for each analyte. The method was also successfully applied to the determination of ethers in surface water samples. The frequent and significant presence of these compounds in the water samples demonstrates a need for further investigations of the aquatic environment in order to establish the distribution and sources of these toxic compounds. The analysis of environmental samples confirm that an effective and validated method able to simultaneously determine hydrophilic ethers such as ETBE, 1,4-dioxane and glymes in environmental samples is necessary in order to conduct an extensive research on the subject. If needed, the method might also be extended to other volatile and semi-volatile ethers of interest.

Chapter 3 Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany.

3.1 Abstract

The behavior of organophosphates and ethers during riverbank filtration and in the anoxic aquifer was assessed to determine their suitability as organic tracers. Four sampling campaigns were conducted at the Oderbruch polder, Germany to establish the presence of chlorinated flame retardants (TCEP, TCPP, TDCP), non-chlorinated plasticizers (TBEP, TiBP, TnBP), and hydrophilic ethers (1,4-dioxane, monoglyme, diglyme, triglyme, tetraglyme) in the Oder River, main drainage ditch, and anoxic aquifer. Selected parameters were measured in order to determine the hydro-chemical composition of both, river water and groundwater. The results of the study confirm that organophosphates (OPs) are more readily attenuated during bank filtration compared to ethers. Both in the river and the groundwater, TCPP was the most abundant OP with concentrations in the main drainage ditch ranging between 105 and 958 ng L^{-1}. 1,4-Dioxane, triglyme, and tetraglyme demonstrated persistent behavior during bank filtration and in the anoxic groundwater. In the drainage ditch concentrations of 1,4-dioxane, triglyme, and tetraglyme ranged between 1090 and 1467 ng L^{-1}, 37 and 149 ng L^{-1} , and 496 and 1403 ng L^{-1}, respectively. A strong positive correlation was found for the inorganic tracer chloride with 1,4-dioxane and tetraglyme. These results confirm the possible application of these ethers as environmental organic tracers. Both inorganic and organic compounds showed temporal variability in the surface – and groundwater. Discharge of the river water, concentrations of analytes at the time of infiltration and attenuation were identified as factors influencing the variable amounts of the analytes in the surface and groundwater. These findings are of great importance for the production of drinking water via bank filtration and natural and artificial

groundwater recharge as the physicochemical properties of ethers create challenges in their removal.

3.2 Introduction

Natural and artificial processes of riverbank filtration are used in many countries in order to replenish groundwater resources that can be subsequently utilized for drinking water production (Tufenkij et al., 2002). Yet in many places, surface waters are not sufficiently shielded from numerous point and nonpoint sources of organic contaminants resulting in a pollution of adjacent aquifers with compounds that are recalcitrant to attenuation through bank filtration. These compounds can play an important role as indicators of anthropogenic groundwater pollution. Several studies have shown contamination of groundwater with trace organic contaminants including organophosphates (OPs) via bank filtration of surface water or artificial recharge using reclaimed water (Knepper et al., 1999; Fries and Püttmann, 2003; Heberer et al., 2004; Stuyfzand et al., 2007; Hoppe-Jones et al., 2010). The presence of ether compounds in bank filtration or artificial recharge sites has also been reported (Noordsij et al., 1985; Schmidt et al., 2003; Achten et al., 2002; Morgenstern et al., 2003; Stuyfzand et al., 2007; Kuster et al., 2010; Kegel et al., 2010; Wiese et al., 2011).

OPs such as the chlorinated flame retardants tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCP) and; the non-chlorinated plasticizers tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP), are industrial chemicals widely used worldwide**.** Since the 1940s, OPs have been added to industrial and consumer products as flame retardants and plasticizing agents. Their use increased significantly between 1960 and 1980 (Muir, 1984). An estimate, made in 2006 by the European Flame Retardant Association (EFRA) indicated that approximately 91,000 tons of OPs were used annually in the EU. Concerns about the potential environmental risks of OPs in aquifer systems have been raised due to their adverse health effects. TCEP, TDCP, and TnBP are classified as category 3 human carcinogens (European chemical substances information system; ECSIS), and TCPP is considered to be a possible human carcinogen (Reemtsma et al., 2008). In order to protect drinking water sources from non or weak genotoxic compounds, the German Environmental Agency has suggested a general precautionary limit of 0.1 µg/L (Umweltbundesamt, 2003). No individual limits exist for the OPs selected for the present study.

The solvents 1,4-dioxane, monoethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) are used in a wide range of industrial processes and products. The current production volumes and applications in Europe are not readily available. Until 1995, 1,4-dioxane was commonly used as a 1,1,1-trichloroethane stabilizer, which was found to deplete the ozone layer and was consequently regulated under the Montreal Protocol (Doherty, 2000). As of 1997, the production volume was estimated to reach 2,000–2,500 tons (European Commission, 2002). Moreover, 1,4-dioxane may form as a by-product of the polyester esterification and ethoxylation process in surfactant production (Zenker et al., 2003). Glycol dimethyl ethers (glymes) are generally used as reaction solvents in the area of pharmaceutical production and manufacture of specialty chemicals. According to the Organization for Economic Co-operation and Development and ECSIS, production of monoglyme and diglyme exceeds 1,000 tons per year in at least one member country (European Chemicals Agency, 2011a, 2011b). In 2002, the Oxygenated Solvent Producer Association reported the production of triglyme to surpass 1000 tons (European Chemicals Agency, 2011c). Production volume of tetraglyme has not been reported by EU industries. Toxicology studies reveal that glymes are toxic to the reproductive and/or developmental systems causing infertility and harm to the unborn children. The International Agency for Research on Cancer (IARC) listed 1,4-dioxane as a possible carcinogen to humans (U.S. EPA, 2011). At this time no water regulatory limits exist in the European Union for the selected ethers studied. The general precautionary limit of 0.10 µg/L set by the German Environmental Agency applies to 1,4-dioxane as it is a non or weak genotoxic compound.

Physicochemical properties of the studied analytes are summarized in **Table 3.1**. Differences in the physicochemical properties of OPs are caused by specific moieties in the organic ester functional groups. The water solubility of OPs is relatively high, ranging from 18.1 mg L^{-1} for TDCP to 7820 mg L^{-1} for TCEP. The values of the *n*-octanol/water partition coefficients (log P_{ow}) and the solid/water partition coefficients for soils (log P_{oc}) range from 1.7 (TCEP) to 4.0 (TnBP) and from 2.48 (TCEP) to 5.67 (TBEP), respectively (Verbruggen et al., 2005). The mobility of TCEP and TCPP is reported to be intermediate-to-high in groundwater, whereas the mobility of TDCP and TBEP is quite low (Pitt et al., 1999; World Health

Organization, 2000; European Commission, 2006, 2007a, 2007b). Unlike chlorinated OPs, the non-chlorinated OPs are expected to be partially degradable in aquatic environments (Saeger et al., 1979; Kawagoshi et al., 2002). However, the behavior of these compounds in groundwater can vary considerably from that in other aquatic compartments because of differences in redox conditions (Amy and Drewes, 2007). Low water temperatures, marginal dilution effects, and low levels of microbial activity can increase the persistence of trace organic contaminants in groundwater resulting in long residence times (Díaz-Cruz and Barceló, 2008), whereas some biogeochemical redox processes can enhance their transformation processes (Borch et al., 2009). Adsorption, dilution, and biological transformation are the most important processes attenuating OPs in groundwater during bank filtration. These processes have been studied with reference to attenuation of OPs in sewage treatment plants (Bester and Schäfer, 2009; Rauch-Williams et al., 2010) and are only poorly understood in the context of surface water infiltration into groundwater through both artificial and natural processes. Results of previous studies on OP stability, biotransformation, and adsorption in soils and groundwater have been inconsistent (Heberer et al., 2004; Amy and Drewes, 2007; Bester and Schäfer, 2009; Rauch-Williams et al., 2010). Some studies have reported a removal of OPs due to adsorption other due to biodegradation. In the field studies, OP elimination was highly dependent on the boundary conditions at the field site.

The ether compounds selected for this study are highly hydrophilic due to their excellent miscibility in water and low log P_{ow}. The negative log P_{ow} values indicate negligible potential for bioaccumulation and a favored partitioning to the soil moisture (Schwarzenbach et al., 1983). Volatilization of all the ethers from aqueous solutions and soil moisture into the air is negligible due to low Henry´s law constants (1.07×10^{-6} to 1.04×10^{-14}). Furthermore, ether bonds generally show low biodegradability in water under both aerobic and anoxic conditions (Kameya et al., 1995; Grossmann et al., 2001). Anticipated processes of ether attenuation during bank filtration are dilution, dispersion, and only possibly biodegradation.

TABLE 3.1 Physicochemical properties of the analyzed OPs and ethers.

Analyte	**CAS No.**	**Molecular weight ($g\ mol^{-1}$)**	**Water solubility (at 25°C; $g\ L^{-1}$)**	**Vapor pressure (mm Hg at 25°C)**	**Henry`s law constant ($atm\times m^3\times mol^{-1}$)**	**Log P_{ow}**	**Log P_{oc}**
Monoglyme	110-71-4	90.1	85.2	79.20	1.07×10^{-6}	−0.21	0.63
1,4-dioxane	123-91-1	88.1	101.5	38.10	4.88×10^{-6}	−0.27	0.60
Diglyme	111-96-6	134.2	162	3.01	5.23×10^{-7}	−0.36	0.45
Triglyme	112-49-2	178.2	208.8	0.24	4.88×10^{-12}	−0.76	0.14
Tetraglyme	143-24-8	222.3	263.9	< 0.01	1.04×10^{-14}	−1.03	< 0
TCEP	115-96-8	285.5	7.82	1.13×10^{-8}	2.55×10^{-8}	1.70	2.48
TCPP	13674-84-5	327.6	1.08	1.38×10^{-8}	5.96×10^{-8}	2.60	2.76
TDCP	13674-87-8	430.9	0.18	5.53×10^{-11}	2.62×10^{-9}	3.80	4.09
TBEP	78-51-3	398.5	1.30	1.62×10^{-9}	1.20×10^{-11}	3.80	5.67
TnBP	126-73-8	266.3	0.40	4.59×10^{-6}	3.19×10^{-6}	4.00	3.28
TiBP	126-71-6	266.3	0.27	1.69×10^{-5}	3.19×10^{-6}	3.60	3.05

U.S. EPA (2011b), European Commission (2006), Verbruggen et al. (2005), IUCLID (2011)

P_{ow} – *n*-octanol/water partition coefficient, P_{oc} – organic carbon partition coefficient

The main objective of this study was 1. to establish the transport behavior of OPs in the groundwater in comparison to the ethers; 2. to discuss possible processes of attenuation of chlorinated and non-chlorinated OPs as well as hydrophilic ethers during bank filtration; and 3. to determine if these compounds are suitable for conservative tracer studies. Three sampling campaigns were conducted at the Oderbruch polder between October 2009 and May 2012. Each time river water, main drainage ditch, and groundwater samples from six shallow and six deep monitoring wells were analyzed to investigate the behavior of OPs and ethers in the aquifer.

3.3 Area description and methods

3.3.1 Site description

The Oderbruch polder is located about 60 km northeast of Berlin and covers an area of more than 800 km². The eastern boundary of the German part of the Oderbruch polder is the Oder River, whereas the western boundary is the till plateau of Barnim/Lebus. Large parts of the polder area are intensively used for agriculture, and therefore influenced by significant hydraulic and water management measures. Levee construction, damming, and drainage with ditches and pumping stations enabled intensive land use over recent centuries. The hydrological environment is characterized by permanent bank filtration of Oder River water into the aquifer. The unrestrained hydraulic contact between river and groundwater and the hydraulically permeable river base lead to a constant groundwater movement towards the slightly inclined polder area. The mostly confined groundwater drains into a wide drainage network encompassing the entire region. The hydraulic situation is thought to have been consistent over the last 250 years (Massmann et al., 2004). The aquifer at Oderbruch polder has an average thickness of 25 m and is composed of fine to medium sized sands of Pleistocene glaciofluvial origin. The aquifer is covered by a 0.2–4.0 m thick largely impermeable layer of Holocene alluvial loam (Massmann et al., 2003). The aquifer base is attached to a Saalian till. Even under low water level conditions Oder River water infiltrates into the bank (flow velocity 0.5–1.5 m d^{-1}), whereas more than 80 % of the filtrate discharges several months later into a main drainage ditch running parallel to the river levee situated 100–200 m from the river (Merz et al., 2005). Bank filtrate travel times from the river to the central polder located about 3500 m from the Oder River are in the order of decades to 120 years (Sültenfuß and Massmann, 2004).

Groundwater from a transect comprising of six shallow (7–10 m) and six deep (19–23 m) groundwater monitoring wells was sampled at the Oderbruch polder (Bahnbruecke site) on four occasions between 2009 and 2012. **Figure 3.1** depicts a simplified geological cross section of the sampling site. Each sampling location consists of one deep and one shallow screened well that allows to distinguish spatial differences in the hydrochemistry and the hydraulic conditions of the groundwater system (Sültenfuß and Massmann, 2004). The identification code, grid value, sampling depth, and distance to the Oder River for each monitoring well are shown in **Table 3.2**. Field parameters (i.e., pH, temperature, conductivity, dissolved O_2, redox potential) were measured at each well using a flow cell equipped with probes. Sampling of groundwater (1 L) was performed in duplicate after all field parameters had stabilized.

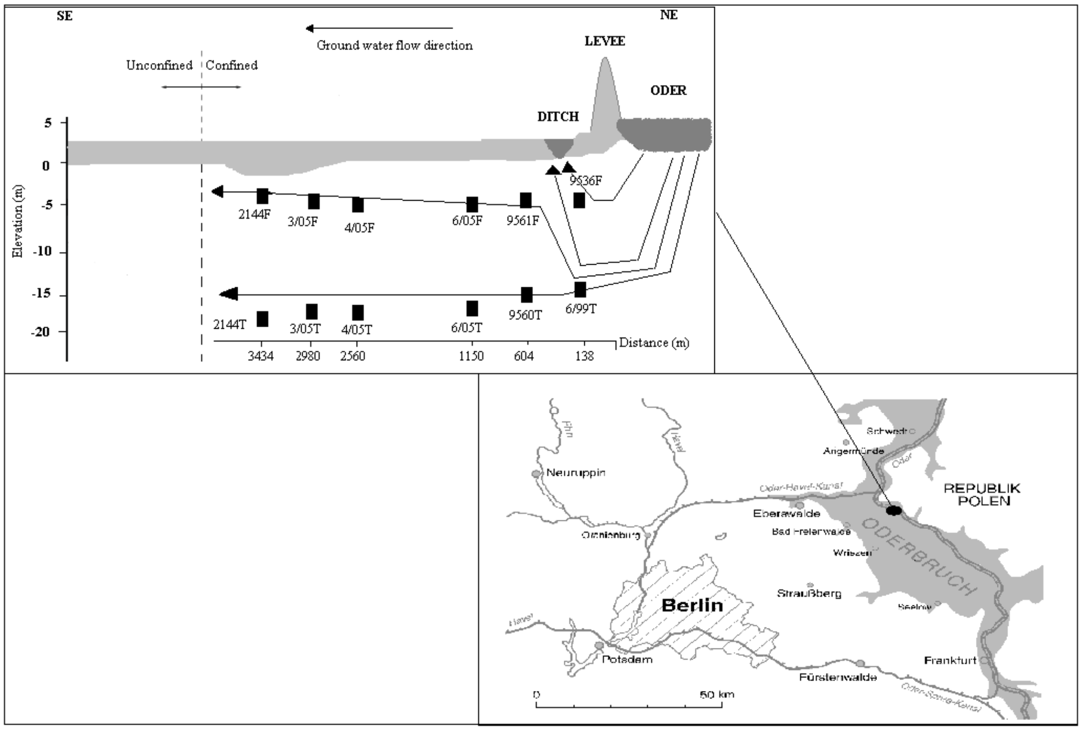


FIGURE 3.1 Location of the Oderbruch polder northeast of Berlin and a simplified geological cross section of the sampling site. The black boxes represent the observation wells sampled. The annotation T stands for deep and the annotation F for shallow well. The arrows indicate groundwater flow direction.

TABLE 3.2 ID codes of the monitoring wells, grid values, sampling depth, distance to the Oder River and groundwater age (apparent $^{3}H/^{3}He$ age) at Oderbruch polder, Germany.

ID	N°	E°	Depth [m]	Distance to river [m]	Apparent age [a][a]
6/99 T	52°48,7980´	14°13,0820´	19.6	138	2.1
9536 F	52°48,7810´	14°13,0580´	7.0	138	3.3
9560 T	52°48,5420´	14°12,9370´	20.0	604	3.0
9561 F	52°48,5400´	14°12,9380´	7.0	604	21.0
6/05 F	52°48,2320´	14°12,8030´	9.0	1150	41.9
6/05 T	52°48,2320´	14°12,8030´	22.0	1150	5.9
4/05 T	52°47,7820´	14°11,7720´	22.0	2560	34.9
4/05 F	52°47,7820´	14°11,7700´	9.6	2560	36.4
3/05 T	52°47,6960´	14°11,5390´	22.0	2980	36.0
3/05 F	52°47,6960´	14°11,5390´	9.0	2980	34.3
2144 T	52°47,4440´	14°11,0890´	23.0	3434	42.4
2144 F	52°47,4390´	14°11,0930´	9.0	3434	44.4

[a] Sültenfuß and Massmann (2004), Tosaki et al. (2007), Massmann et al. (2009).

3.3.2 Analytical methods

Method I: A detailed description of the analytical method for the determination of OPs using gas chromatography–mass spectrometry (GC–MS) is provided in references Regnery and Püttmann (2009; 2010). Hence, only a brief description is given. This method was also used to analyze triglyme and tetraglyme during the 2011 sampling. Groundwater samples (1 L) were not filtered prior to the solid phase extraction (SPE). The samples were extracted using a styrene–divinylbenzene polymeric SPE cartridge (Bond Elute PPL, 1 mL; Varian, Darmstadt, Germany), which was eluted with 1 mL methanol/acetonitrile (1/1 v/v). Quantitative analyses of the target compounds in the sample extracts were performed using a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany) operating in full scan mode (50-600 *m/z*). A TR-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness; Thermo Scientific) was used for GC separation with the following temperature program: 80 °C for 1 min, increase to 300 °C at 4 °C min^{-1}, final temperature kept for 25 min.

Target analytes were quantified using squalane (Sigma Aldrich, Steinheim, Germany) as an internal calibration standard (Regnery and Püttmann, 2009). Individual stock solutions (1 µg μL^{-1}) of TCEP, TiBP, TnBP, TBEP, tetraglyme (Sigma Aldrich), TCPP, TDCP (Akzo Nobel, Amersfoort, The Netherlands), and triglyme (Alfa Aeser, Karlsruhe, Germany) were prepared in methanol/acetonitrile (1/1 v/v), whereas squalane stock solution (1 µg μL^{-1}) was prepared in hexane. Acetonitrile (J. T. Baker, Deventer, The Netherlands) was ultrapure HPLC grade and was used as received. All other solvents (Merck, Darmstadt, Germany) were of analytical grade and were distilled before use. Working standard solutions were obtained by appropriate dilution. All stock and working standard solutions were regularly renewed every 2-4 weeks.

Method II: The samples obtained during the 2012 sampling were analyzed for 1,4-dioxane, monoglyme, diglyme, triglyme, and tetraglyme with a SPE GC–MS method that has been developed especially for the six hydrophilic ether compounds (Stepien and Püttmann, 2013). Resprep® Coconut charcoal SPE cartridges (Restek, 80-120 mesh, approx. 150 µm) were used to extract and enrich the analytes from the water samples. Surrogate (1,4-dioxane-d_8, 1 µg μl^{-1}) was added to each sample resulting in a final concentration of 500 µg L^{-1}. The analytes were eluted with 10 mL of dichloromethane. 10 µL of internal standard 4–chlorotetrahydropyran (12.5 µg L^{-1}) was added to 500 µL extract and the sample vials were placed in the Combi PAL autosampler (CTC Analytics, Switzerland). Two µL of extract was injected onto the Trace 2000 gas chromatograph coupled to a Voyager mass spectrometer (ThermoQuest Finnigan). The GC was equipped with a DB-624 column (Agilent, Waldbronn, Germany) and the following temperature program applied: 37 °C for 2.5 min, increased to 75 °C at 4 °C min^{-1} and 10 °C min^{-1} to the final temperature of 220 °C, kept for 10 min. The standard stock solution (1 µg μL^{-1}) of 1,4-dioxane(Ultra Scientific, Kingstown, USA), diglyme (Dr. Ehrenstorfer, Ausgburg, Germany), monoglyme (Sigma Aldrich), triglyme, and tetraglyme was prepared in methanol (hypergrade, Merck). The working standards were prepared by appropriate dilution with distilled dichloromethane.

The analyses of groundwater hydrochemistry were performed at the Institute of Landscape Hydrology at the Leibniz-Centre for Agricultural Landscape Research (ZALF e.V.). Water samples were analyzed for Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, NO_3^-, NO_2^- and SO_4^{2-} by ion chromatography (DX500, Dionex, Idstein, Germany) using an IonPac column CS12A for the cations and an AS9-HC4 column for the anions. Iron was determined by inductively coupled plasma atomic emission spectroscopy (Jobin Yvon, Unterhaching, Germany), alkalinity was determined by titration and NH_4^+ and PO_4^{2-} were measured by photometry (SPECORD 200, Analytik Jena, Jena, Germany).

3.3.3 Quality assurance

Samples were collected in 1 L amber glass bottles, which were thoroughly pre-cleaned prior to sampling to avoid sample contamination. The samples were extracted within 72 h of collection. As controls for possible contamination during transport and laboratory treatment, blanks of ultrapure water were included and treated identically to the collected samples. Concentrations were not corrected in terms of SPE recovery rates. Recoveries of OPs in ultrapure water (n = 6) and natural surface water (n = 3) were in the range of 85–99 % and 72–99 %, respectively, with relative standard deviations (RSD) less than 10 %. Triglyme and tetraglyme demonstrated a recovery range of 87-98 % in ultrapure water (n = 5) with relative SD less than 7 %. Limits of detection (LOD) of 1 ng L^{-1} for TCEP, TCPP, TDCP, TBEP, TnBP, TiBP, and tetraglyme (Method I), and 2 ng L^{-1} for triglyme (Method I) were calculated from seven-point calibration curves of standard mixtures in accordance with DIN 32645 (DINTest, University of Heidelberg, α = 1 %). For TCEP, TCPP, TiBP, TnBP, triglyme, and tetraglyme the limit of quantification (LOQ) was estimated as three times the LOD, and ranged from 3 ng L^{-1} for TCEP to 5 ng L^{-1} for triglyme. As TDCP (4 ± 6 ng L^{-1}) and TBEP (3 ± 5 ng L^{-1}) were detected in the blanks (n = 8), the LOQ for each compound was calculated as the mean of blank value plus six times the SD of the mean, resulting in LOQs of 40 ng L^{-1} (TDCP) and 33 ng L^{-1} (TBEP). The LOD for the ethers using coconut charcoal SPE extraction and the Voyager GC-MS were calculated according to the United States Environmental Protection Agency Chapter 40 part 136, Appendix B of the Federal Register (U.S. Environmental Protection Agency, 2011c). Eight replicates of the environmental water samples (Main River) were spiked at 40 ng L^{-1}, extracted and analyzed in order to calculate the following LODs: Monoglyme, 4 ng L^{-1}; 1,4-dioxane, 16 ng L^{-1}; diglyme, 13 ng L^{-1}; triglyme, 10 ng L^{-1}; and tetraglyme, 12 ng L^{-1}. The LOQs were determined by multiplying the average SD of the replicate analysis by 10, resulting in LOQs for each compound between 12 and52 ng L^{-1}.

3.4 Results and discussion

3.4.1 Hydrochemistry

Geochemical indicators of natural attenuation can help to identify the ongoing processes in the aquifer. A more detailed description of the redox processes in the Oderbruch polder is provided by Massmann et al. (2004). **Figure 3.2** shows average values for the redox relevant parameters in Oder River water (n = 1; March 2011) and deep groundwater wells (n = 3). Groundwater redox potentials (E_h) varied between samplings but were on average below 100 mV. As shown in **Figure 3.2**, both dissolved O_2 and NO_3^- were consumed between the river and the first deep sampling well revealing anoxic conditions in the groundwater. The dissolved organic carbon (DOC) dropped from 7.6 mg L^{-1} (n = 1) to 6.3 mg L^{-1} (n = 3). The decrease in DOC continued until the deep well located 604 m away from the surface water body and slowly increased to 8.4 mg L^{-1} in the last well (3434 m). The pH decreased gradually with distance from the Oder River (pH 7.62 at well 6/99 T to pH 6.89 at well 2144 T). The electrical conductivity of the groundwater decreased with increasing distance from the river. Sulfate concentration increased in the groundwater flow direction (75.5 to 127 mg L^{-1}). A significant sulfate drop in the most distant deep groundwater well (49.9 mg L^{-1}; well 2144 T) indicates a sulfate–reducing environment. A continuous increase in dissolved iron (Fe(II)) from 0.05 mg L^{-1} in the first well to more than 15 mg L^{-1} over a distance of 2980 m (well 3/05 T) points to the occurrence of iron reduction throughout the aquifer (**Figure 3.2**).

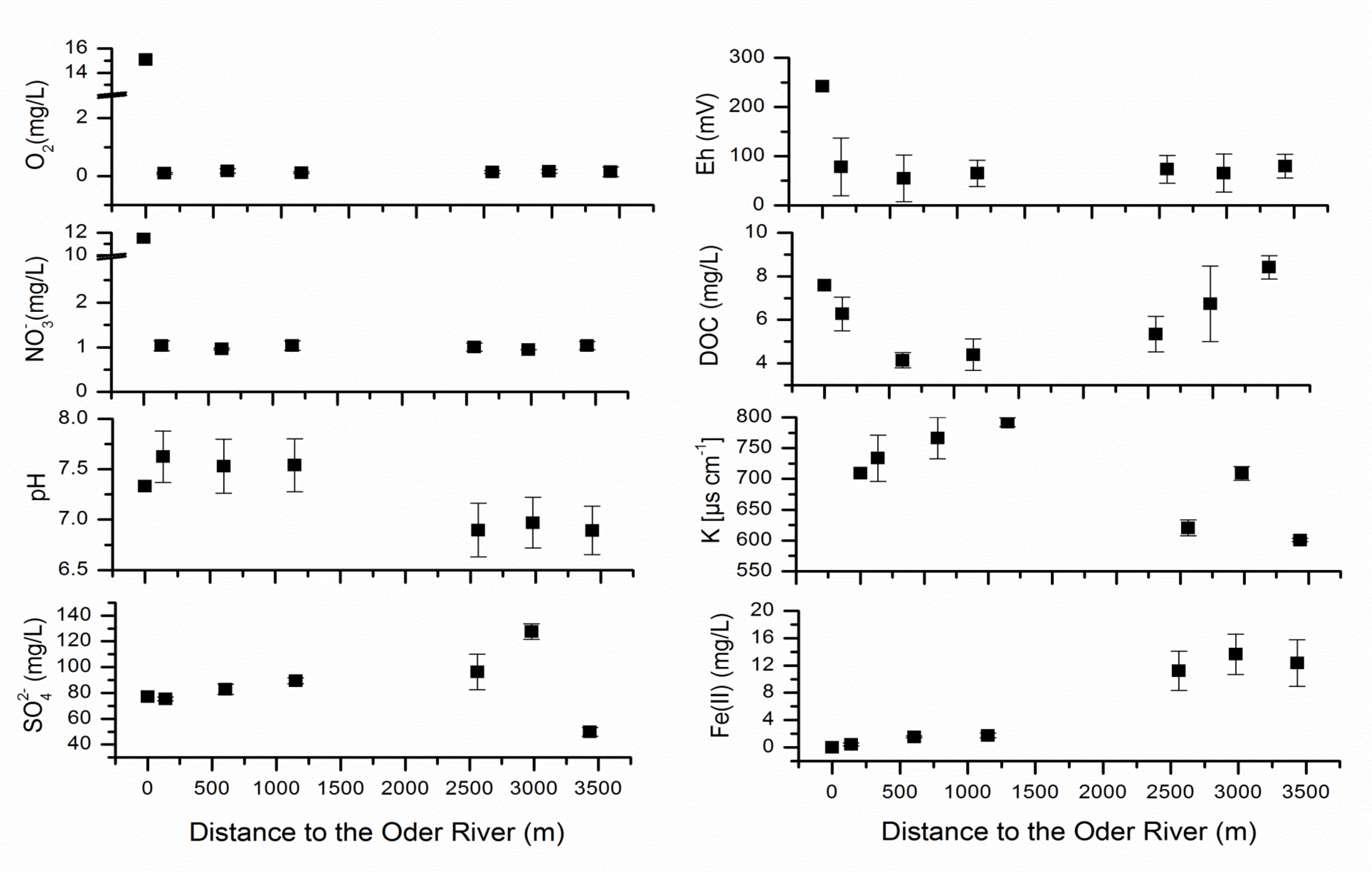


FIGURE 3.2 Concentration of redox relevant parameters in the Oder River (n = 1) and six deep groundwater wells (n =3): redox potential (Eh), dissolved organic carbon (DOC), pH, conductivity (K), oxygen (O_2), nitrate (NO_3^-), ferrous iron (Fe(II)) and sulfate (SO_4^2).

3.4.2 Infiltration of OPs and ethers into the main drainage ditch

Table 3.3 summarizes the results of four sampling campaigns carried out between October 2009 and May 2012. Concentrations of OPs and ethers detected in the Oder river, the drainage ditch (following bank filtration), and seven groundwater sampling wells of the Bahnbruecke transect comprising of three shallow and four deep groundwater wells are listed. Based on the results collected temporal variations in the concentrations and compounds identified in the river and the main drainage ditch are apparent.

Except for TnBP, every OP was detected in the Oder River during each of the samplings conducted. Following bank filtration, in the main drainage ditch, TBEP and TDCP were not present. These two OPs have the highest *n*-octanol/water partition coefficients and are expected to sorb to soil particles (both log $P_{ow} = 3.8$) during infiltration. TiBP was the only non-chlorinated plasticizer detected in the ditch and the groundwater, although at low concentrations. Its concentration in the surface water ranged from 4 to 54 ng L^{-1} and in the main drainage ditch from 2 to19 ng L^{-1}. Most abundant OPs in the Oder River were two chlorinated flame retardants TCEP (7-540 ng L^{-1}) and TCPP (123-2353 ng L^{-1}). In the drainage ditch their concentrations decreased to 9-171 ng L^{-1} and 105-958 ng L^{-1}, respectively.

Ethers were also readily identified in the collected samples. Triglyme was present during all of the sampling campaigns in both river and drainage ditch at 20-185 ng L^{-1} and 37-149 ng L^{-1}, respectively. Tetraglyme was detected at high concentrations both in the Oder River (273-1576 ng L^{-1}) and the ditch (496-1403 ng L^{-1}). During the 2012 campaign, water samples were additionally analyzed for monoglyme, diglyme, and 1,4-dioxane with Method II. Monoglyme was not detected in any of the water samples. Diglyme was present in the river at lower concentrations compared to other glymes detected. In the river water its concentration ranged between 65 and 94 ng L^{-1} and in the ditch between 23 and 41 ng L^{-1}. 1,4-Dioxane greatly exceeded in abundance all other analyzed compounds, with concentrations ranging from 1610 to 3290 ng L^{-1} in the Oder River and 1090 to 1467 ng L^{-1} in the ditch.

TABLE 3.3 Concentrations of OPs and ethers (ng L^{-1}) in the Oder River, adjacent main drainage ditch as well as shallow (F) and deep (T) groundwater sampling wells.

Analyte	Sampling Date	Oder River	Ditch	9536 F	9561 F	6/05 F	6/99 T	9560 T	6/05 T	4/05 T
TiBP	27.10.09	54	19	12			4	6	5	
	10.03.11	4	2	4			BDL	BDL	BDL	
	27.03.12	18	4	7			3	7	6	
	23.05.12	12	9	18			15	28	26	
TCPP	27.10.09	2353	958	261			291	66	31	
	10.03.11	183	198	324			201	36	14	
	27.03.12	123	128	258			206	54	23	
	23.05.12	217	105	406			355	92	55	
TDCP	27.10.09	BDL								
	10.03.11	7								
	27.03.12	7								
	23.05.12	5								
TBEP	27.10.09	BDL								
	10.03.11	43								
	27.03.12	63								
	23.05.12	12								
Triglyme	27.10.09	151	106	245			98	74	19	
	10.03.11	20	37	82			38	35	25	
	27.03.12*	173	100	68			67	104	131	
	23.05.12*	185	149	241			86	125	153	
Tetraglyme	27.10.09	1260	1230	1849	BDL		1230	849	442	
	10.03.11	273	496	803	29		350	369	212	
	27.03.12*	1433	693	547	60		455	520	565	
	23.05.12*	1576	1403	1464	50		496	630	741	
1,4-dioxane*	27.03.12	1610	1467	1440	751	196	1340	1020	1630	208
	23.05.12	3290	1090	740	1040	121	1060	901	1129	219
Diglyme*	27.03.12	94	41	34			31	26		
	23.05.12	65	23	BDL			29	BDL		

* Analyzed by Coconut charcoal SPE and Voyager GC/MS
BDL− below detection limit

The concentrations of ethers both in the river and the main drainage ditch were typically higher in comparison to OPs. The elevated use and poor removal techniques in the wastewater treatment plants might account for their increased presence in the surface water (Vainberg et al., 2006). The high concentrations of ethers (i.e. triglyme, tetraglyme, and 1,4-dioxane) following bank filtration can be related to their vast water solubility and poor sorption to soils (Barker et al., 1990). From the investigated OPs, only TCPP was present at significantly high concentrations (>

100 ng L^{-1}) in the main drainage ditch. Among the investigated OPs, TCPP and TCEP are expected to be the least affected by the attenuation processes during bank filtration.

3.4.3 Occurrence of OPs and ethers in the aquifer

The groundwater from shallow wells near the Oder River (well 9/99 F and 9536 F) is hydraulically affected by the drainage function of the main ditch (**Figure 3.1**), therefore only groundwater from the six deep monitoring wells (19–23 m deep; **Table 3.2**) reaches beyond the ditch and represents an undisturbed water transport in the aquifer (Tosaki et al., 2007). The groundwater ages provided were determined in a study conducted by Massmann et al. (2009) using $^{3}H/^{3}He$ technique and match perfectly the modeled hydraulic ages up to the distance of 1150 m.

In the deep wells of the Oderbruch polder TiBP, TCEP, and TCPP have been detected at varying concentrations up to the groundwater age of 5.9 years (well 6/05T, **Table 3.2 and 3.3**). In March 2011, TiBP was not detected above its detection limit in the groundwater, however in the 2009 and 2012 samplings the concentration of TiBP in the deep groundwater wells increased with water age, indicating a decrease in its use in over 6 years (**Table 3.3**). This decline is confirmed by low river concentrations between 2009 and 2012. TCEP and TCPP were present at generally lower concentrations during 2011 sampling in the deep groundwater wells (4-20 ng L^{-1} and 14-201 ng L^{-1}) as compared to 2009 and 2012 samplings (9-51 ng L^{-1} and 23-355 ng L^{-1}). In general, concentrations of OPs in the groundwater in May 2012 were higher than in the sampling performed two months earlier, whereas trends between deep groundwater wells remained similar. In 2009 and 2011, TCEP concentration decreased with groundwater age. In 2012 its concentration was higher in the 3 year old groundwater (9560 T) compared to the preceding 6/99 T well (2.1 years), decreasing again in the final well (6/05T, 5.9 years) where the compound was detected. These patterns reflect the variability of TCEP concentration in the river during the last decade. The infiltration and transport of TCPP from the river into the aquifer differed compared to other OPs. Its concentration in the aquifer dropped sharply between the groundwater age of 2.1 and 3.0 years, a strong indication for attenuation in the anoxic aquifer.

The use of the chlorinated flame retardants TCEP and TCPP did not markedly increase until the 1970s (Muir, 1984). In Germany, both compounds were used in equal proportions in polyurethane foams until the mid-90s, when TCEP was phased out in Europe following a voluntary industry agreement (Leisewitz et al., 2001). Although TCEP is no longer expected to be utilized as flame retardant in the European industry, it is still present in surface waters at fluctuating levels. TCEP has been recently detected in both house dust samples from California, as well as polyurethane foam samples collected from couches in the US (Stapleton et al., 2012; Dodson et al., 2012). These findings document that TCEP still enters the environment via evaporation from flame protected products that are produced outside the EU, but also same source of the chlorinated flame retardants might exist in Europe.

The concentration of triglyme and tetraglyme decreased with groundwater age during the 2009 and 2011 sampling campaigns, while in 2012, the concentrations increased with groundwater age. This pattern suggests that concentration of glymes has been increasing in the last decade, considering the residence time of the groundwater in this part of transect. Tetraglyme was also detected in the shallow well (9561 F) with an estimated groundwater age of 21 years (27-60 ng L^{-1}), indicating its long-term entrance into the groundwater. The anticipated onset of triglyme and tetraglyme might be due to the increasing contribution of treated and/or untreated effluents of industrial origin, but based on their extensive applications the source is difficult to identify at this time. It is clearly visible from the acquired results that triglyme and tetraglyme persist in the anoxic groundwater and are not markedly degraded. 1,4-Dioxane was present at significant concentrations (> 200 ng L^{-1}) up to the deep well 4/05 T with the estimated groundwater age of 34.9 years (2560 m). In the groundwater between 2.1 and 6 years its concentration exceeded 1000 ng L^{-1}. The drop in the amount of 1,4-dioxane between well 6/05 T and 4/05 T can be attributed to lower historical concentrations in the surface water as well as dispersion of groundwater (see section 3.4.6). The ability to determine 1,4-dioxane in such distant and old groundwater clearly demonstrates its resistance to attenuation by the bank filtration process and the anoxic conditions in the aquifer.

3.4.4 Factors influencing OP and ether concentrations

In addition to the residence time of the river water during bank filtration and the expected retardation of a compound, the highly variable concentrations in the river at the time of infiltration control contaminant dynamics in the groundwater following bank filtration (Noordsij et al., 1985). During winter time, many contaminants tend to be diluted by increased natural discharges, such as rain and snow. Whereas during a dry season, the river water is expected to have the highest concentration of contaminants, due to the lesser dilution of effluents coming from the domestic and industrial wastewater treatment (Heberer et al., 2004). **Figure 3.3** depict the changing levels and volume rate of water flow (discharge, in m^3 s^{-1}) of the Oder River between January 2006 and May 2012 at Hohensaaten-Finow (river km 664.9), which is located in the proximity to the sampling area (Landesamt für Umwelt, Gesundheit und Verbraucherschutz [LUGV], 2012).

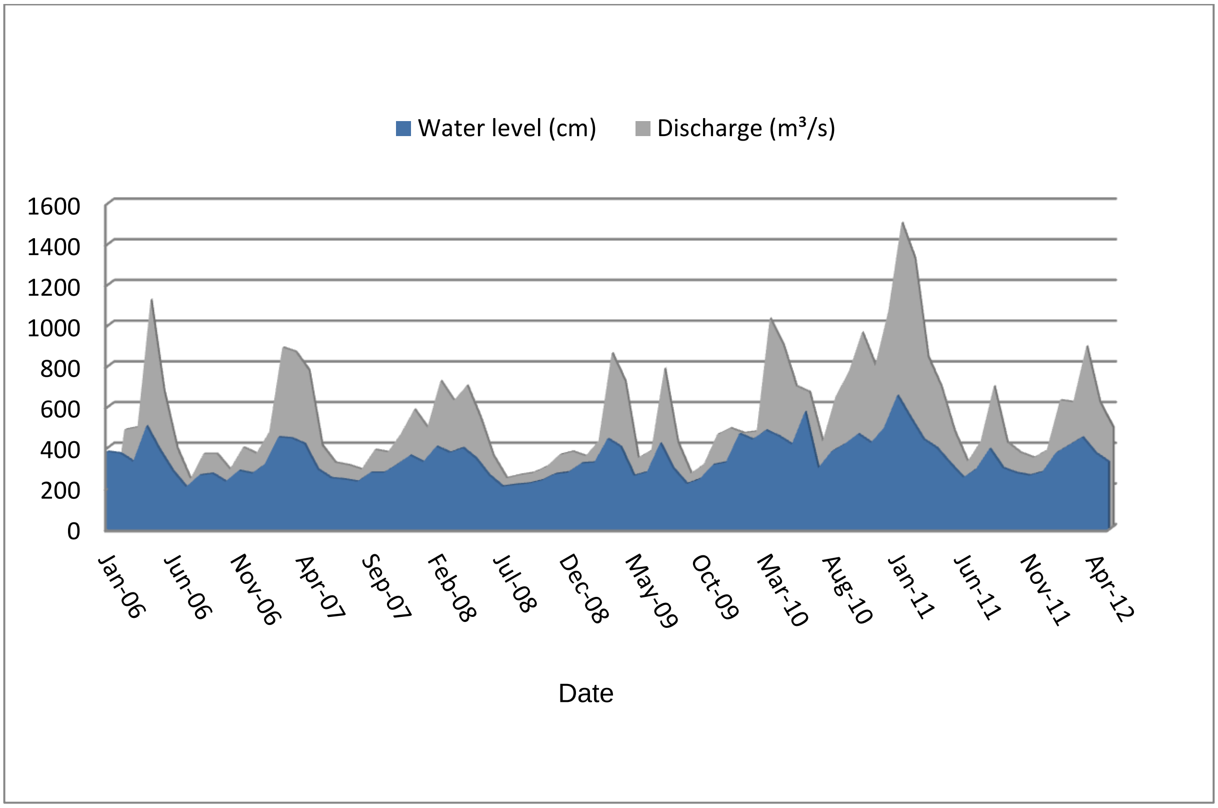


FIGURE 3.3 Average monthly water level (cm) and mean flow (discharge, m^3 s^{-1}) of the Oder River between January 2006 and May 2012 at the Hohensaaten-Finow monitoring station (LUGV, 2011).

Based on the **Figure 3.3** the increased discharge of the Oder River is especially apparent in the winter months. In the **Figure 3.4** graphical comparison of the OP and ether concentrations to the discharge of the Oder River during four sampling campaigns is presented. During March 2011 sampling, the extremely high discharge rates in the Oder River at the end of 2010 and early months of 2011 can explain the low concentrations of some analytes in the river (i.e. TCEP, triglyme, and tetraglyme; **Table 3.3**). At that time (discharge, 813 m^3 s^{-1}), concentrations of TCEP, TCPP, triglyme, and tetraglyme in the main drainage ditch exceeded the concentrations in the Oder River. Only the concentration of TCPP remained high in the river during the increased water levels, proposing its entrance with surface runoff from urban areas close to the river (Regnery and Püttmann 2009; 2010).

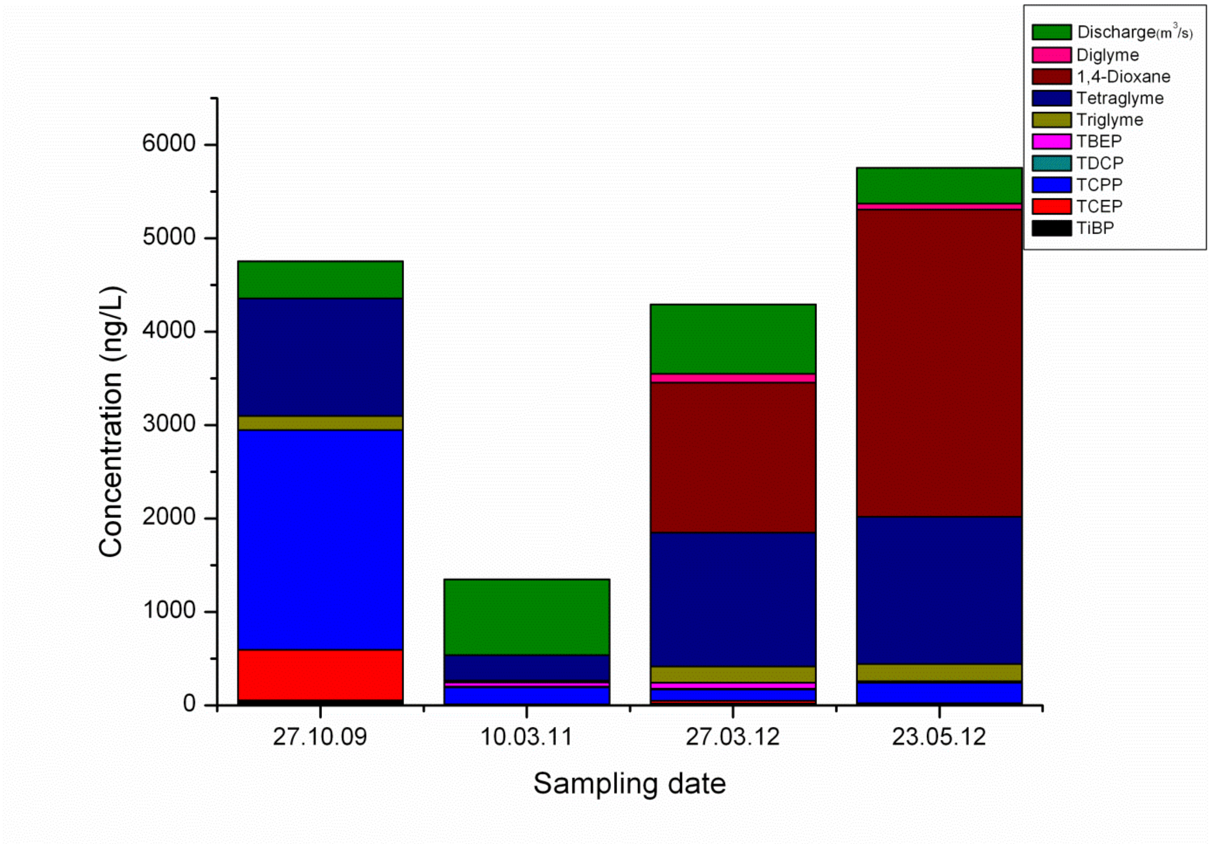


FIGURE 3.4 Variations of OP and ether concentrations (ng L^{-1}) with discharge (m^3 s^{-1}) of the Oder River during four sampling campaigns. Diglyme and 1,4-dioxane were only analyzed in the samples collected on 20.03.2012 and 23.05.2012.

In 2009 (discharge, 397 m^3 s^{-1}) concentrations of TiBP, TCEP, and TCPP were extremely high compared to the levels observed during successive samplings. Possibly these OPs entered the surface water as a result of the high precipitation in the summer months (seen as a high peak in July–August 2009, **Figure 3.3**). In 2012, the concentrations of TiBP, TCEP, TDCP, and TBEP varied with the discharge rate. In March, when the discharge rate was 740 m^3 s^{-1} concentrations were higher than in May when discharge dropped to 381 m^3 s^{-1}. The opposite is true for TCPP, which almost doubled in May 2012. Glymes were present in the river at similar concentrations during the samplings conducted in 2009 and 2012 and they did not respond to varying discharge rates. In contrast, the amount of 1,4-dioxane in the river doubled with the drop in a discharge rate. The abovementioned results suggest that the concentrations of OPs and ethers in the aquifer are generally controlled by the fluctuating input from the Oder River.

3.4.5 Attenuation of OPs and ethers during bank filtration

The proportion of analyte removal through bank filtration can only be calculated if the respective surface water concentrations at the time of infiltration are known. Nevertheless, the results of the study confirm that during bank filtration processes OPs are more readily attenuated compared to ethers. Based on the acquired data, attenuation of the studied compounds is discussed.

Non-chlorinated organophosphates are expected to be less stable than chlorinated OPs in an aquifer as a result of biotransformation processes. Elimination rates of up to 89 % have been reported for TnBP and TBEP during bank filtration and in soil infiltration experiments (Schmidt, 2005; Bester and Schäfer, 2009). In the Oderbruch polder, TBEP was removed by the bank filtration processes below detection limit, confirming its efficient biodegradation. Sorption of chlorinated OPs on soils has been reported to be a function of the soil organic carbon content, and sorption to soil components other than organic carbon has been suggested to be insignificant (European Commission, 2007b). Such behavior can also be assumed for the non-chlorinated OPs, explaining the presence of TiBP in both the drainage ditch and groundwater. Of all the non-chlorinated OPs considered in this study TiBP is expected to be attenuated the least by sorption to soil. According to the modeled Freundlich parameters, TDCP is considerably better adsorbed to organic carbon surfaces than is TCPP or TCEP (Nowotny et al., 2007). In this study concentration of TDCP in the river was low, and it was not present above detection limit in the drainage ditch following bank filtration. In the riverbank filtration study of Hoppe-Jones et al. (2010) no changes in concentrations of TCEP and TCPP were observed during subsurface treatment. Slight seasonal variations were reported for TCEP, with concentrations below 200 ng L^{-1} in the winter and above 200 ng L^{-1} in the summer (Hopee-Jones et al., 2010). In the Oderbruch polder, both TCEP and TCPP were not removed by the bank filtration and were eliminated below detection limit after 6 year residence time in the groundwater, proving their resistance to rapid biodegradation. The organic carbon composition of the river bed and the hyporheic zone is of major importance in the removal of OPs during river–aquifer interactions. Depending on sedimentation conditions, the concentrations of total organic carbon (TOC) in Oder River sediments vary between 0.2 % and 11.0 % (Duft et al., 2002). The aquifer at the

Oderbruch polder consists of fine-to-medium-sized sands and sediments, and contains less than 0.1 % TOC (Massmann et al., 2004). However, high concentrations of organic matter in the top layer of river sediments (i.e. dirt cover, biofilm) and in soils near rivers will enhance the sorption of OPs within the first few centimeters-to-meters during subsurface transport of percolating river water. Adsorption of trace organic pollutants is significantly reduced in the presence of background organic matter (i.e., DOC) (Nowotny et al., 2007). At Oderbruch polder, the DOC value increased from 6.3 mg L^{-1} at site 6/99 T near the Oder River to 8.4 mg L^{-1} in groundwater at well 2144 T, far from the river. Further work will be necessary to clarify whether groundwater contains degradation products (e.g., bi- and mono-alkyl phosphates) of chlorinated and non-chlorinated OPs. Knowledge of the processes of transformation and/or degradation of these analytes in groundwater is rudimentary.

Results of this study indicate that ethers are not easily adsorbed or degraded during infiltration of surface water. Their high water solubility and low soil partitioning coefficient prevents them from volatilization and adsorption to aquifer material. Triglyme, tetraglyme and 1,4-dioxane were present at significantly high concentrations following bank filtration. Concentrations of diglyme in the surface water and main drainage ditch were lower, but also this glyme showed little degradation during bank filtration. As a consequence of the polar characteristics of ethers, these and similar compounds (e.g. MTBE) migrate through the aquifer with minimal retardation (Achten et al., 2002; Deeb et al., 2003). Initial degradation studies of MTBE under anaerobic conditions found that it is recalcitrant under sulfate-reducing conditions, and very poorly degraded under nitrate-reducing conditions (Mormille et al., 1994). More recent studies provided evidence of MTBE degradation in anoxic environment under nitrate-reducing, sulfate-reducing, iron-reducing, and methanogenic conditions (Bradley et al., 2001a; Bradley et al., 2001b; Finneran and Lovely, 2011). However, a study focusing on the biodegradation of 1,4-dioxane under these hydro-geochemical settings showed no degradation in anaerobic microcosms during more than 400 days of incubation (U.S. Department of Defense, 2007). Biodegradation of ethers under methanogenic conditions require very low sulfate concentrations, whereas mineralization of ethers due to denitrification is limited by nitrate availability and only expected to occur in contaminated aquifers. In the Oderbruch aquifer, sulfate reduction occurred in the last sampling well, 3434 m from the river (**Figure 3.2**). No ethers were present in such distant well. According to **Figure 3.2**, denitrification occurred between the river and the first deep groundwater well (6/99 T). Therefore these two processes are not expected to contribute to the degradation of ethers in the Oderbruch. The high iron (II) concentrations in the groundwater are the result of a reduction of Fe (hydr)-oxides in the sediment of the aquifer (Massmann et al., 2004). Numerous studies focused on 1,4-dioxane decomposition in the presence of iron species in the sludge, wastewater, and contaminated groundwater (Beckett and Hua, 2003; Kiker et al., 2010; So et al., 2009; Shen et al., 2008). In order to observe significant reduction or removal of the compound, strong oxidizing agents in the form of hydrogen peroxide or humic acid have to be supplied. The ex-situ studies suggest the development of anaerobic microbial communities capable of 1,4-dioxane degradation, since Fe (II) is often present in the groundwater contaminated with 1,4-dioxane (Shen et al., 2008). As determination of ether degradation products was not a part of the current study, it cannot be confirmed if iron reduction enhanced the attenuation of 1,4-dioxane in the groundwater. Based on the concentrations detected and chemical characteristics of 1,4-dioxane and glymes, only dispersion and dilution will be considered as relevant attenuation processes during riverbank filtration and groundwater movement in the Oderbruch polder. As concluded by Landmeyer et al. (1999) these are possibly the most effective processes in the reduction of trace organic contaminants such as ethers.

3.4.6 Organic pollutants as hydrological tracers

A substance unintentionally released and persistent in the environment can become useful as a hydrological tracer. Ideally such pollutant should move with the water, without sorption to soil and without degradation (Flury and Wai, 2003). Moreover the chosen tracer should be resistant to changes in pH, alkalinity, or ionic strength, and should be easily detected in trace amounts by chemical analysis. The ideal groundwater tracer does not exist, but when different tracers are simultaneously determined, groundwater characteristics can be adequately identified. Chloride (Cl^-) ion is often used as conservative inorganic tracer to study groundwater dynamics (Basberg et al., 1998; Lee et al., 2001; Peters et al., 1998). Cl^- is highly mobile due to its negligible sorption and minor chemical interactions with other materials during bank filtration process (Cox et al., 2007). Numerous sources affect the presence of Cl^- in the surface water and consequently in the groundwater such as: irrigation runoff, sewage effluents, precipitation, mining, chemical industry, snowmelt, and road salting during the winter (Department of Natural Resources Indiana, 2002). Temporal variability in chloride concentration in both the Oder River and in the groundwater was determined during this and previous studies study (Massmann, 2002).

Persistent pollutants present at significant concentrations in the groundwater can be potentially applied as environmental tracers, therefore only OPs and ethers present at concentrations close to 100 ng L^{-1} were considered. Concentration of TCPP in the 2.1 year old groundwater exceeded 200 ng L^{-1}, but after 3 year groundwater residence time its concentration decreased by 74−82 %. Obviously TCPP is affected by biological and/or chemical processes in the aquifer. Therefore only triglyme, tetraglyme, and 1,4-dioxane were evaluated as possible environmental tracers. Consequently, the presence of these compounds was correlated to the inorganic tracer Cl^{-}. Relationship of triglyme with Cl^{-} concentration resulted in a relatively scattered pattern, which limits its use as organic tracer; nevertheless this glyme remains a good indicator of groundwater contamination. **Figure 3.5** demonstrate a good correlation of 1,4-dioxane (r = 0.913) and tetraglyme (r = 0.613) to Cl^{-}concentration in the river water and deep groundwater wells.

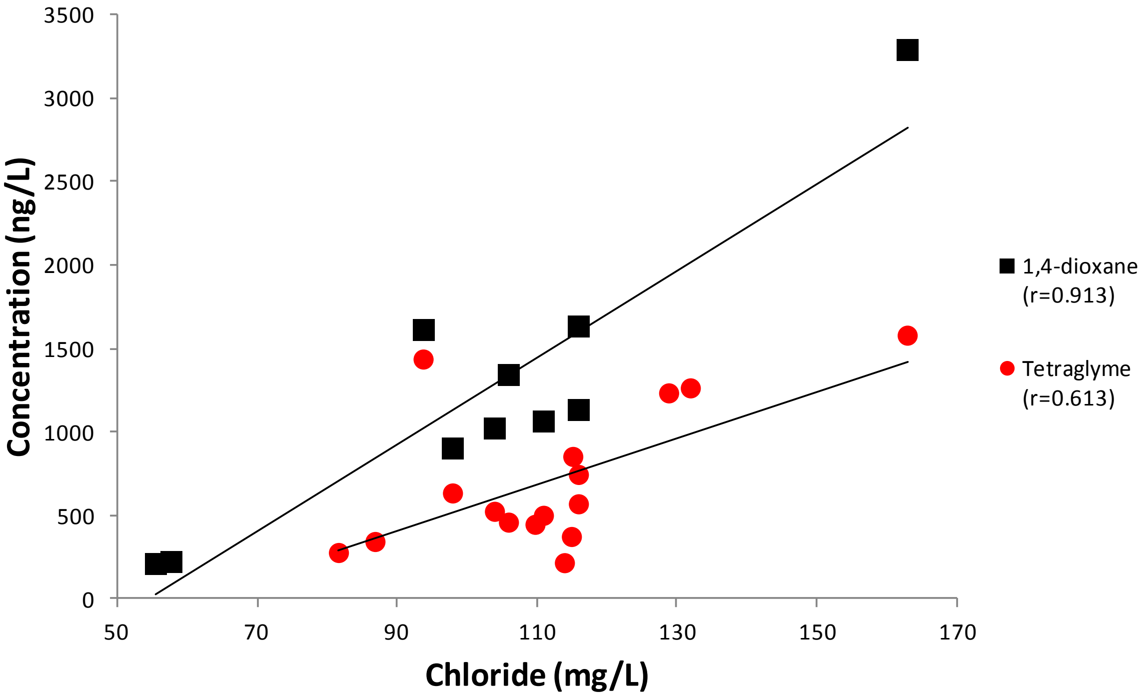


FIGURE 3.5 Correlation between chloride (mg L^{-1}), 1,4-dioxane, and tetraglyme (ng L^{-1}) concentrations in the Oder River and deep groundwater wells during four sampling campaigns. Correlation coefficients (r) for chloride with the ethers are given in parenthesis.

The only points deviating strongly from the linearity occurred in March 2012 in the Oder River for both ethers. The chloride value for this sampling was taken five days prior to the actual sampling for the ether determination (93.8 mg L^{-1}) and may possibly differ from the actual concentration on the sampling day. Also during 2011 sampling, the low concentrations of tetraglyme relatively to chloride (114 mg L^{-1}) caused divergence. Nevertheless, similarities in the behavior of Cl^{-} and the organic compounds suggest that 1,4-dioxane and tetraglyme are controlled by the same hydraulic process and therefore can be used as additional tracers to study the dynamics of the groundwater system.

3.5 Conclusions

In the Oderbruch polder, the presence of one non-chlorinated OP (TiBP) and two chlorinated OPs (TCEP, TCPP) was determined in the main drainage ditch following bank filtration and in the anoxic aquifer. Moreover, the great mobility and low degradation potential were shown for hydrophilic ethers (diglyme, triglyme, tetraglyme, and 1,4-dioxane). Under the aquifer conditions described TiBP, TCEP, TCPP, diglyme and triglyme are not suitable as organic tracers in groundwater, because of their low and fluctuating concentration and/or biodegradation. Nevertheless, they are good indicators of contamination of groundwater with organic contaminant loaded surface waters. 1,4-Dioxane and tetraglyme were both present at significant concentrations (above 100 ng L^{-1}) in the river, main drainage ditch and aquifer. Their persistence in the groundwater with an estimated age of 21 to 42 years, confirms their low biodegradation in the anoxic aquifer. The decrease in concentrations of both ethers and chloride at more distant groundwater wells is attributed to lower historical concentrations in the Oder River and the dispersion of the groundwater. The strong correlation of 1,4-dioxane and tetraglyme with the inorganic tracer Cl^{-} confirms their behavior as organic tracers. Therefore, 1,4-dioxane and tetraglyme can play an important role in the interpretation of substance flow dynamics in complex groundwater systems. In order to exclude biodegradation of ethers in the aquifer, the formation of degradation products needs to be investigated.

Chapter 4 Fate of 1,4-dioxane in the aquatic environment: from sewage to drinking water

4.1 Abstract

Potential health effects of 1,4-dioxane and the limited data on its occurrence in the water cycle command for more research. In the current study, mobility and persistence of 1,4-dioxane in the sewage-, surface-, and drinking water was investigated. The occurrence of 1,4-dioxane was determined in wastewater samples from four domestic sewage treatment plants (STP). The influent and effluent samples were collected during weekly campaigns. The average influent concentrations in all four plants ranged from 262 ± 32 ng L^{-1} to 834 ± 480 ng L^{-1}, whereas the average effluents concentrations were between 267 ± 35 ng L^{-1} and 62,260 ± 36,000 ng L^{-1}. No removal of 1,4-dioxane during water treatment was observed. Owing to its strong internal chemical bonding, 1,4-dioxane is considered non-biodegradable under conventional bio-treatment technologies. The source of increased 1,4-dioxane concentrations in the effluents was identified to originate from impurities in the methanol used in the postanoxic denitrification process in one of the STPs. In view of poor biodegradation in STPs, surface water samples were collected to establish an extent of 1,4-dioxane pollution. Spatial and temporal distribution of 1,4-dioxane in the Rivers Main, Rhine, and Oder was examined. Concentrations reaching 2,200 ng L^{-1} in the Oder River, and 860 ng L^{-1} in both Main and Rhine River were detected. The average load during the sampling was estimated to be 6.5 kg d^{-1} in the Main, 34.1 kg d^{-1} in the Oder, and 134.5 kg d^{-1} in the Rhine River. In all rivers, concentration of 1,4-dioxane increased with distance from the source and was found to decrease with the increasing discharge of the river. Additionally, bank filtration and drinking water samples from two drinking water facilities were analysed for the presence of 1,4-dioxane. The raw water contained 650 ng L^{-1} to 670 ng L^{-1} of 1,4-dioxane, whereas the concentration in the drinking water fell only to 600 ng L^{-1} and 490 ng L^{-1}, respectively. Neither of the purification processes applied were able to reduce the presence

of 1,4-dioxane below the precautionary guideline limit of 100 ng L^{-1} set by the German Federal Environmental Agency.

4.2. Introduction

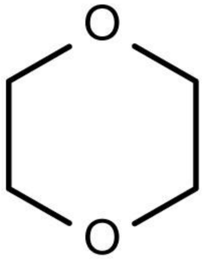
1,4-Dioxane is a polar cyclic diether, commonly used as an industrial solvent in the production of adhesives, paint strippers, dyes, degreasers, fabric cleaners, paper, electronics, and pharmaceuticals (Tanabe et al., 2006). In the past, 1,4-dioxane was mainly associated with its use as a solvent stabilizer especially for 1,1,1-trichloroethane (1,1,1-TCA). This application was discontinued in the 1990s, when 1,1,1-TCA was banned by the Montreal Protocol, due to its ozone depleting properties. Moreover, 1,4-dioxane is unintentionally formed during several chemical processes used to produce soaps, polyester, and plastics. According to the European Chemical Substances Information System, 1,4-dioxane is a high production volume chemical, meaning production exceeds 1,000 tons per year in at least one member country. The European Union Risk Assessment Report from 2002, states that the only production site in Europe; BASF SE in Ludwigshafen, Germany produced 2,000 – 2,500 tons of 1,4-dioxane in 1997. Currently, European Chemicals Agency lists three registrants/suppliers in Europe: BASF SE and Merck KGaA in Germany and Sustainability Support Services (Europe) AG in Sweden with a total amount of 1,4-dioxane exceeding 100 tons per year.

In recent years international concern has risen about the ubiquitous presence of 1,4-dioxane in the environment and the adverse health effects to its exposure. United States Environmental Protection Agency (U.S. EPA) and the International Agency for Research on Cancer assigned 1,4-dioxane to group B2 as a possible human carcinogen. Toxicological studies revealed an increased incidence of nasal cavity and liver carcinomas in rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs (Zenker et al., 2003). Since then, a number of international regulatory guidelines emerged for 1,4-dioxane. World Health Organization suggested a 50 µg L^{-1} drinking water threshold value for 1,4-dioxane, whereas the U.S. EPA National Center for Environmental Assessment proposed a health-based advisory level of 3 µg L^{-1} in the tap water (Mohr, 2010). According to the U.S. EPA Integrated Risk Information System, cancer development could occur in 1 out of 1,000,000 people exposed to a concentration of 350 ng L^{-1} in drinking water over a lifetime (75 years). As a result, Unregulated Contaminant Monitoring Regulation from 2012, proposed a minimum reporting level for 1,4-dioxane at 70 ng

L^{-1}. In its Drinking Water Regulation (2001), the German Federal Environmental Agency suggested a precautionary guideline limit for weak or non genotoxic compounds such as 1,4-dioxane at 100 ng L^{-1} in drinking water.

The physiochemical properties of 1,4-dioxane govern its high mobility and persistence in the environment (**Table 4.1**). Based on Henry's law constant (4.88×10^{-6} atm × m^3 × mol^{-1}) and the indefinite solubility in water, volatilization of 1,4-dioxane from water is expected to occur slowly (National Industrial Chemicals Notification and Assessment Scheme [NICNAS], 1998). The low octanol water coefficient ($\log P_{ow} = -0.27$) is in accordance with its high mobility in soil and leaching to groundwater as well as no significant adsorbance to suspended sediments. The moderate vapor pressure and Henry's law constant implies slow volatilization from moist soil; however fast volatilization from dry soils. When 1,4-dioxane enters the atmosphere it is subjected to photo oxidation with hydroxyl radical (*OH) radicals with a half-life of less than 7 hours (NICNAS, 1998). Based on the aforementioned properties, removal of 1,4-dioxane from wastewater is expected to be difficult, increasing the possibility of surface, groundwater, as well as drinking water contamination.

TABLE 4.1 Physicochemical properties and the structure of 1,4-dioxane.

Property	Value	Reference	Structure
Molecular weight (g/mol)	88.1	Budavari et al. (1989)	
Density (g/cm^3)	1.033	Keith and Walters (1985)	
Boiling point (°C at 760 mmHg)	101.1	Verschueren (1983)	
Water solubility (at 25°C; g/L)	Miscible	Budavari et al. (1989)	
Vapor pressure (mmHg at 20°C)	30	Verschueren (1983)	
Henry's law constant (atm×m ^{3}/mol^{-1})	4.88×10^{-6}	Howard (1990)	
Partition coefficient (Log P_{ow})	-0.27	Howard (1990)	
$\log P_{oc}$	0.54	Howard (1990)	

Data on the present dispersion of 1,4-dioxane in the environment in Europe and around the world are not readily available. Already, three decades ago 1,4-dioxane was first found as a water contaminant in the US (Kraybill, 1978; Burmaster, 1982; Hartung, 1989). Most recent work focussed on distribution of 1,4-dioxane in polluted groundwaters (Isaacson, 2006; Chiang, 2008). Also, in Canada, groundwater contamination with the ether was documented (European Commission, 2002; Lesage, 1990). In Europe, the presence of 1,4-dioxane was confirmed in surface waters in Germany, Netherlands, and in the United Kingdom (European Commission, 2002; Gelman Sciences, 1989). Moreover, 1,4-dioxane was detected in a municipal landfill leachate in Sweden as well as in the industrial wastewater from polyester resin producing company (Paxéus, 2000; Romero et al., 1998). In Japan, extensive research on the distribution and occurrence of 1,4-dioxane has been carried out. Numerous studies confirmed the presence of 1,4-dioxane in landfill leachate (Yasuhara et al., 2003; Fujiwara et al., 2008), effluents from sewage plants (Abe, 1999; Tanabe et al., 2006), surface and groundwater (Abe, 1999; Kawata et al., 2003, Kawata and Tanabe, 2009). Other studies focused on the investigation of 1,4-dioxane in non-ionic surfactants and cosmetics. Fuh et al. (2005) determined that 22% of daily use cosmetics in Taiwan contained between 4.2 ppm and 41.1 ppm of 1,4-dioxane. Black et al. (2001) reported up to 1410 ppm of 1,4-dioxane in ethoxylated raw materials and up to 279 ppm in cosmetic finished products. Numerous studies on the presence of 1,4-dioxane in cosmetic products have been conducted by independent consumer organizations in both US and Europe.

In the presented study, the occurrence and distribution of 1,4-dioxane in the aquatic environment in Germany and Poland is investigated. The focus of the current study was to examine the mobility of 1,4-dioxane from wastewater to surface water, bank filtered groundwater, and finally to drinking water plants. The extent of 1,4-dioxane removal through riverbank filtration, drinking water treatment, and wastewater treatment was also investigated. To the best of our knowledge this is the first study conducted in Europe that focuses primarily on the occurrence and transport of 1,4-dioxane in such a wide range of samples from the aquatic environment.

4.3. Materials and methods

4.3.1. Chemicals and reagents

1,4-Dioxane (99.5 %, CAS No. 123-91-1) was purchased from Ultra Scientific (Kingstown, USA). 1,4-Dioxane-d_8 (99 %, CAS No. 17647-74-4) was used as a surrogate (SU) and 4-chlorotetrahydropyran (96 %, CAS No. 1768-64-5) as an internal standard (IS). Both standards were obtained from Sigma-Aldrich (Steinheim, Germany). Analytical grade dichloromethane (DCM) and hypergrade methanol, used for extraction and standard preparation, were purchased from Merck (Darmstadt, Germany). DCM was distilled before use. To produce ultrapure water, the Astacus water purification system from MembraPure (Bodenheim, Germany) was used. Sodium bisulfate, a microbial inhibitor, was purchased from Aldrich Chemistry (Steinheim, Germany). Anhydrous sodium sulfate was supplied by Sigma Aldrich (Seelze, Germany) and conditioned at 400°C for 4 h before use. Separate stock solutions of 1 µg μL^{-1} of 1,4-dioxane, SU, and IS were prepared in methanol. Subsequent working standards were obtained through appropriate dilutions in DCM.

4.3.2 Analytical methods

The method used for determination of 1,4-dioxane in water samples has been previously described in detail by Stepien and Püttmann (2013) and U.S. Environmental Protection Agency (2008). Therefore, only a short description of the extraction and analytical method follows. Two solid-phase extraction (SPE) methods were used to determine 1,4-dioxane in water samples. The first method involved "Resprep® activated coconut charcoal SPE cartridges" (Restek, 80-120 mesh, approximately 150 µm, 2 g, 6 mL) and 500 mL of water sample loaded onto the previously conditioned adsorbing material with DCM, methanol, and distilled water. The elution of the analyte was accomplished with 10 mL of DCM. The second method required only 100 mL of a water sample to be passed through a conditioned "Supelclean™ ENVI-Carb™ Plus" SPE tube (Supelco, bed wt. 400 mg, 1 mL). Prior to the elution, cartridges were washed with 2 mL of 20 % methanol solution. Analytes of interest were eluted with 2 mL dichloromethane. The extracts were then dried on the sodium sulfate column. After each extraction, 500 µL of an extract and 10 µL of IS are added (0.125 µg μL^{-1}, 4-chlorotetrahydropyran) and placed in the autosampler for GC/MS analysis. Only influent samples obtained from wastewater treatment plant were subjected to pressure filtration before extraction, to prevent clogging of the cartridges. For that purpose a stainless steel pressure holder (2.12 L; Sartorius, Goettingen, Germany) equipped with a 142 mm diameter borosilicate glass fiber filter (Filter pore size <1 µm; type A/E, Pall, Dreieich, Germany) was used, with 1.5 bar air pressure. Before use, the filters were conditioned in DCM and heated to 400 °C for 2 h. After each blank, spike, and sample filtration the equipment was thoroughly cleaned with ultrapure water.

Analyses were carried out using a Thermo Finnigan Voyager MS system coupled to a Trace 2000 GC (ThermoQuest Finnigan, Dreieich, Germany) equipped with a DB-624 column (30 m length, 0.25 mm ID, 1.40 µm film thicknesses) from Agilent (Waldbronn, Germany). The injector temperature was set at 240°C in 1 min splitless mode. The column temperature program started at 37 °C for 2.5 minutes, increased at the rate of 4 °C min^{-1} to 75 °C with the final 10 °C min^{-1} increase to 220 °C. Carrier gas, helium (≥99.99 %) was set to a constant flow mode of 1 mL min^{-1}. The mass spectrometer was operated in a selected ion monitoring mode with electron impact ionization set to 70 eV. For data processing XCalibur software (Thermo Fisher Scientific, version 2.0.7) was used. Quantitation of 1,4-dioxane was performed using an internal standard method. The response factor for 1,4-dioxane was calculated relatively to 4-chlorotetrahydropyran at seven calibration levels ranging in concentration from 2.0 µg L^{-1} to 250 µg L^{-1} (corresponding to 0.040 – 5.0 µg L^{-1} in the sample). SU and IS were added at 500 µg L^{-1} and 250 µg L^{-1}, respectively.

4.3.3. Quality assurance

Amber glass collection containers were pre-cleaned with distilled water and methanol and heated in the oven at 110 °C for a minimum of two hours to ensure no contamination of the sample. Preservative in the form of sodium bisulfate was added to each bottle at 1 g per Liter. After collection, the samples were stored in the refrigerators during transport and in the refrigerated storage room at 4 °C prior to the extraction. Each sample was extracted after a maximum of 8 days from the collection day. A method blank and control standards were included with each batch of 17 samples. Prior to the extraction, samples, blanks, and control standards were enriched with 5 µL of a surrogate (1.0 or 0.20 µg $µL^{-1}$). Control samples were spiked with standards to reach the final concentration close to the detection limit and the mid-point of the calibration curve. The percentage of surrogate and spike recovery was always within the acceptable range of 70 % to 130 %. For the method utilizing 500 mL of a sample, 1,4-dioxane recovery in the ultrapure samples spiked at 1.0 µg L^{-1} and 10 µg L^{-1} was calculated to be in the range of 94.3 % to 97.1 % with a relative standard deviation of 3.4 % to 4.1 % (Stepien and Püttmann, 2013). The limit of quantitation (LOQ) for 1,4-dioxane in the surface water samples was determined to be 52 ng L^{-1} and 34 ng L^{-1} in ultrapure water samples (Stepien and Püttmann, 2013). For 100 mL samples, the extraction recovery for 1,4-dioxane was calculated to be 103 % with a relative standard deviation of 4.69 %. The LOQ equaled to 32 ng L^{-1} for ultrapure water samples and 34 ng L^{-1} for surface waters. Additionally, a study was performed to determine the stability of 1,4-dioxane in the ultrapure water and surface waters when preserved with sodium bisulfate. After 10 days, there was no observable decrease in the spiked concentration.

All of the extracts were analyzed in the SIM mode. The presence of 1,4-dioxane in environmental samples was confirmed using the abundance of the confirmation ions (*m/z* = 58, 87) relative to the target ion (*m/z* = 88). The ratio had to agree with the absolute 20 % of the relative abundance in the spectrum taken from the most recent calibration standard analyzed in the SIM mode.

4.5. Site description and sampling methods

4.5.1. Sewage treatment plants

Four municipal Sewage Treatment Plants (STPs) were investigated for the occurrence of 1,4-dioxane. **Table 4.2** lists relevant information about the sampling and the capacity of the STPs. Each STP examined was equipped with fundamental treatment processes such as mechanical pre-treatment with coarse particle screening, an aerated grit-removal tank, a primary clarifier and one to two biological treatment stages with activated sludge. Two of the STPs studied (C, D) employ a postanoxic denitrification step before discharging the effluent into the receiving surface water. In each case, the external carbon source consisted of methanol, to provide an electron donor for nitrate reduction. Influent and effluent water samples were acquired at each STP. Additionally, water samples after primary and secondary treatment were obtained from STP C. Twenty-four hours composite samples were collected at STP B, C, and D for a continuous duration of at least seven days. At STP A, qualified random samples were taken for a week. In STP D, two influents are separately entering the plant, which represent approximately 57 % and 43 % of wastewater, respectively. Each influent is mechanically pretreated, before it is joined together for a first and second biological treatment with a final postanoxic denitrification step. STP A represents the lowest capacity plant (73,000 people served), whereas STP D the highest. The wastewater treated in all of the STPs consisted of household sewage and indirect discharges from industries. STP B receives the highest and STP C the lowest percentage of indirect discharges.

TABLE 4.2 Sampling events and characteristics of the four sewage treatment plants sampled.

	Sewage Treatment Plant			
	A	B	C	D
No. of samples	14	16	42	21
Sampling date	10.12.12-16.12.12	13.11.12-20.11.12	27.11.12-03.12.12 17.01.13-23.01.13	08.07.13-14.07.13
Sampling type	Qualified random sample	24-h composite	24-h composite	24-h composite
Retention time	24-h	48-h		24-h
Flow rate of outflow (m^3 year^{-1})	8,290,000	14,100,000	16,000,000	92,600,000
% of indirect discharge	35	50	30	38
Population served	73,000	240,000	140,000	750,000
Treatment steps	M/B/N/D/P	M/B/N/P	M/B/N/D/P	M/B/N/D/P

M - mechanical, B - biological, N - nitrification, D - denitrification, P - phosphorus removal

4.5.2. Surface waters

For the investigation of 1,4-dioxane in surface waters, three rivers were chosen. The Oder River flows mainly through western Poland, becoming a border between Poland and Germany at river km 545, ultimately flowing into the Baltic Sea. Forty-nine samples (n = 49) were obtained from a 600 km stretch of the river between January 2012 and April 2013. Each collection flask containing sodium bisulfate was filled to the top, leaving no headspace. The samples were collected along the shore line of the river, from the bridges or from a ship where possible. The second surveyed river was the Rhine, which is the longest river in Germany. A two week investigation (08/20/12 and 09/02/12) of the 24-hours composite samples (n = 28) was undertaken at the Rhine Water Control Station Worms, Germany, located at river km 443.3. The sample collection took place on the left (MWL1) and on the right (MWL4) side of the river. Submersible pumps allowed for a collection of water samples from the river at the depth of 50 cm. The sampling systems consisted of two auto-samplers SP II-A (MAXX Mess- und Probennahmetechnik GmbH, Germany) connected to twelve water collectors, keeping the water cooled at 4°C. Throughout the day, 15 mL of water were collected every 10 min. Additionally, over a 350 km stretch of the Rhine River − between the city of Mainz (km 499) and Emmerich (km 852) − was sampled in May 2013 resulting in 19 samples. The Main River being the most significant right tributary of the Rhine River was sampled on April 2013. Fifteen (n = 15) samples were obtained between Hanau and Mainz-Kostheim. **Table 4.3** lists all surface water sampling locations and the corresponding water conditions on the day of the sampling and **Figure 4.1** illustrates the sampling locations.

4.5.3. Bank filtration and drinking water treatment

Two drinking water treatment (DWT) facilities were investigated for the presence of 1,4-dioxane that utilize bank filtered surface water from the Rhine River for the drinking water production. Sample collection of the DWT 1 was performed by an external company on the 12/10/12. A total of 11 water samples were obtained: 9 from multilevel wells, one raw water sample after bank filtration, and a drinking water sample. Three multilevel monitoring wells A (n = 3), B (n = 3), and C (n = 3) are situated 20, 40, and 80 m from the river bank, respectively. In the matter of weeks (15-70 d), surface water passes through a 30 m thick sand and gravel layer where the natural filtration of water occurs. The water reaching wells A and B originates from the bank filtration only. In well C, generally groundwater inflow from land is observed, except at high river water levels when mixing with bank filtration water takes place. Subsequently, the raw water is directed to the DWT plant, where the following treatment processes are implemented to meet drinking water standards: ozonation, aeration, and a two layer activated carbon filtration. Finally, a mix of phosphate and silicate (at 1 mg L^{-1}) and chloride dioxide (at 0.06 mg L^{-1}) are added to the finished water in order to prevent corrosion of the pipes and biological contamination. More information about the area sampled can be found in Achten et al. (2002).

DWT 2 was sampled on the 03/22/13. One river sample, raw water sample, and two drinking water samples were obtained. The facility treats and provides 8 million m^3 of drinking water per year to about 170,000 people. The natural filtration of the surface water takes on average 35 days, until it reaches the recovering well. The naturally pre-cleaned raw water undergoes additional purification steps at the DWT facility. The following treatment processes are utilized: ozonation, oxidation, sand/gravel filtration, activated carbon filtration, physical decalcification to remove carbonic acid, and disinfection with chlorine dioxide.

TABLE 4.3 Sampling locations, sample ID, river water level (cm), and discharge ($m^3 s^{-1}$) during surface water collection from the Oder, Rhine, and Main River.

River	Sample ID	Sampling Location	No. of samples	River km	Level (cm)	Discharge ($m^3 s^{-1}$)	Sampling date
Oder	Od1	Genschmar	1	626			Jan-12
Oder	Od2	Groß-Neuendorf	1	634			Jan-12
Oder	Od3	Güstebieser Loose	1	645	436	806	Jan-12
Oder	Od4	Bienenwerder	1	654	436	806	Jan-12
Oder	Od5	Lebus, DE	1	595	350	370	Mar-12
Oder	Od6	Połęcko, PL	2	530	233	289	Mar-12
Oder	Od7		1	530	77	97.3	Aug-12
Oder	Od8	Frankfurt,DE/Slubice, PL	2	585	141		Aug-12
Oder	Od9	Krosno Odrzańskie	1	514			Aug-12
Oder	Od10	Brody, PL	2	491	142	87.2	Aug-12
Oder	Od11	Nowa Sól, PL	2	429	142	82.4	Aug-12
Oder	Od12		2	429	307	283	Apr-13
Oder	Od13	Bytom Odrzański, PL	1	416			Aug-13
Oder	Od14		1	416			Apr-13
Oder	Od15	Glogów, PL	2	392	157		Aug-13
Oder	Od16		3	392			Apr-13
Oder	Od17	Ścinawa, PL	2	331	151	104	Aug-13
Oder	Od18		3	331	295	263	Apr-13
Oder	Od19	Kawice, PL	2	310			Aug-13
Oder	Od20		1	310	354	291	Apr-13
Oder	Od21	Malczyce, PL	1	305			Aug-13
Oder	Od22	Brzed Dolny, PL	1	284	97-196	61.6-124	Aug-13
Oder	Od23		2	284			Apr-13
Oder	Od24	Wrocław, PL	1	242	314		Aug-13
Oder	Od25	Oława, PL	2	216	177		Aug-13
Oder	Od26	Brzeg, PL	2	199	126		Aug-13
Oder	Od27	Kopanie, PL	1	187			Aug-13
Oder	Od28	Opole, PL	1	155	405		Aug-13
Oder	Od29	Krapkowice, PL	2	124	217		Aug-13
Oder	Od30	Koźle, PL	3	97	276		Aug-13
Oder	Od31	Uraz, PL	1	272			Apr-13
Rhine	Rh1	Worms	28	443	118-241	886-1541	08/20/12-09/02/12
Rhine	Rh2	Guntersblum	1	473			Mar-13
Rhine	Rh3	Nierstein	1	483			Mar-13
Rhine	Rh4	Mainz-Kastel	2	499	402		May-13
Rhine	Rh5	Koblenz	2	591	396		May-13
Rhine	Rh6	Wiesenthurm	2	611			May-13
Rhine	Rh7	Bad Honnef	2	642			May-13
Rhine	Rh8	Bonn	2	655	492	3480	May-13
Rhine	Rh9	Köln	1	688	517	3630	May-13
Rhine	Rh10	Leverkusen	1	699			May-13
Rhine	Rh11	Düsseldorf	2	744	474	3650	May-13
Rhine	Rh12	Ruhrort	2	780	619	3740	May-13
Rhine	Rh13	Wesel	1	814	586		May-13
Rhine	Rh14	Rees	1	837	525	3705	May-13
Rhine	Rh15	Emmerich	1	852	463	3770	May-13
Main	Ma1	Hanau	2	469		156*	Apr-13
Main	Ma2	Maintal	2	474		156	Apr-13
Main	Ma3	Offenbach	2	482		156	Apr-13
Main	Ma4	Schwanheim	2	500		156	Apr-13
Main	Ma5	Höchst	1	503		156	Apr-13
Main	Ma6	Sindlingen	2	506		156	Apr-13
Main	Ma7	Rüsselsheim	2	517		156	Apr-13
Main	Ma8	Mainz-Kostheim	2	526		156	Apr-13

* average discharge of the River Main on the day of the sampling (Source: German Federal Institute of Hydrology (BfG))

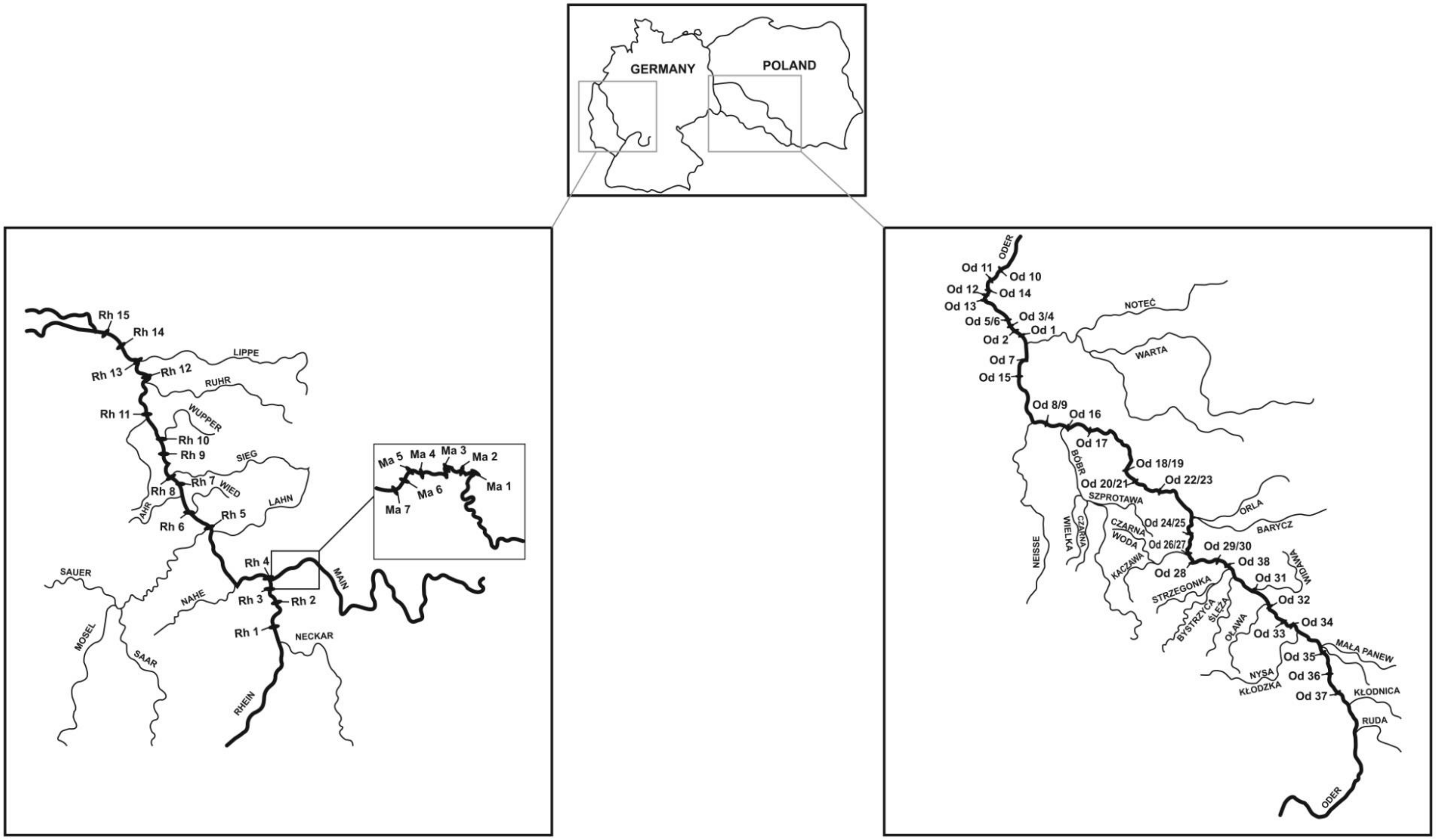


FIGURE 4.1 Maps of surface water sampling sites in Germany and Poland, including major tributaries. Sample IDs reflect the locations listed in Table 4.3.

4.6. Results and discussion

4.6.1. 1,4-dioxane in municipal sewage treatment plants

Four sewage treatment plants (STP) were investigated with respect to the occurrence of 1,4-dioxane in the wastewater coming mainly from the domestic sewage. 1,4-Dioxane was detected in the influent and effluent samples at each STP. Additionally, samples after primary and secondary treatment were collected at STP C. The concentrations of 1,4-dioxane in the wastewater from each STP are presented in **Figure 4.2**. In the STP A, B, and D the average concentration of 1,4-dioxane (n = 7 - 8) in the influent was 262 ± 32 ng L^{-1}, 340 ± 62 ng L^{-1}, and 516 ± 73 ng L^{-1}, respectively. The lowest average concentration of 1,4-dioxane was detected in the STP A, which also has the lowest capacity. In the STP C the average influent concentration based on 14 collected samples was 833 ± 480 ng L^{-1}. In STP A, B, and D the concentrations in the effluents were comparable to those detected in the influents, showing that the wastewater treatment steps are not configured for 1,4-dioxane removal. In comparison, STP C effluent contained extremely high amount of 1,4-dioxane (62,260 ± 35,960 ng L^{-1}). In this STP, effluent concentrations were over 100 times higher than in the influent. Based on the daily average discharge at the STP C, the load of 1,4-dioxane into the receiving surface water was calculated to be 0.59 -2.51 kg d^{-1} during December sampling and 2.17 – 5.03 kg d^{-1} in January. The second weekly sampling campaign was therefore extended to wastewater samples after primary and secondary treatment, where the average concentrations were 6,120 ± 2,420 ng L^{-1} and 5,800 ± 2,490 ng L^{-1}, respectively.

The potential sources of 1,4-dioxane within the water treatment process at STP C were inspected. The increased concentrations after primary and secondary treatment and the extremely high concentrations in the effluent, supported the assumption that methanol used in the postanoxic denitrification step might be responsible for the increased concentrations of 1,4-dioxane. Hence methanol samples were obtained both from STP C and D for analysis. Three different lots of methanol provided by two different suppliers were obtained from STP C and two different lots of methanol were made available by STP D.

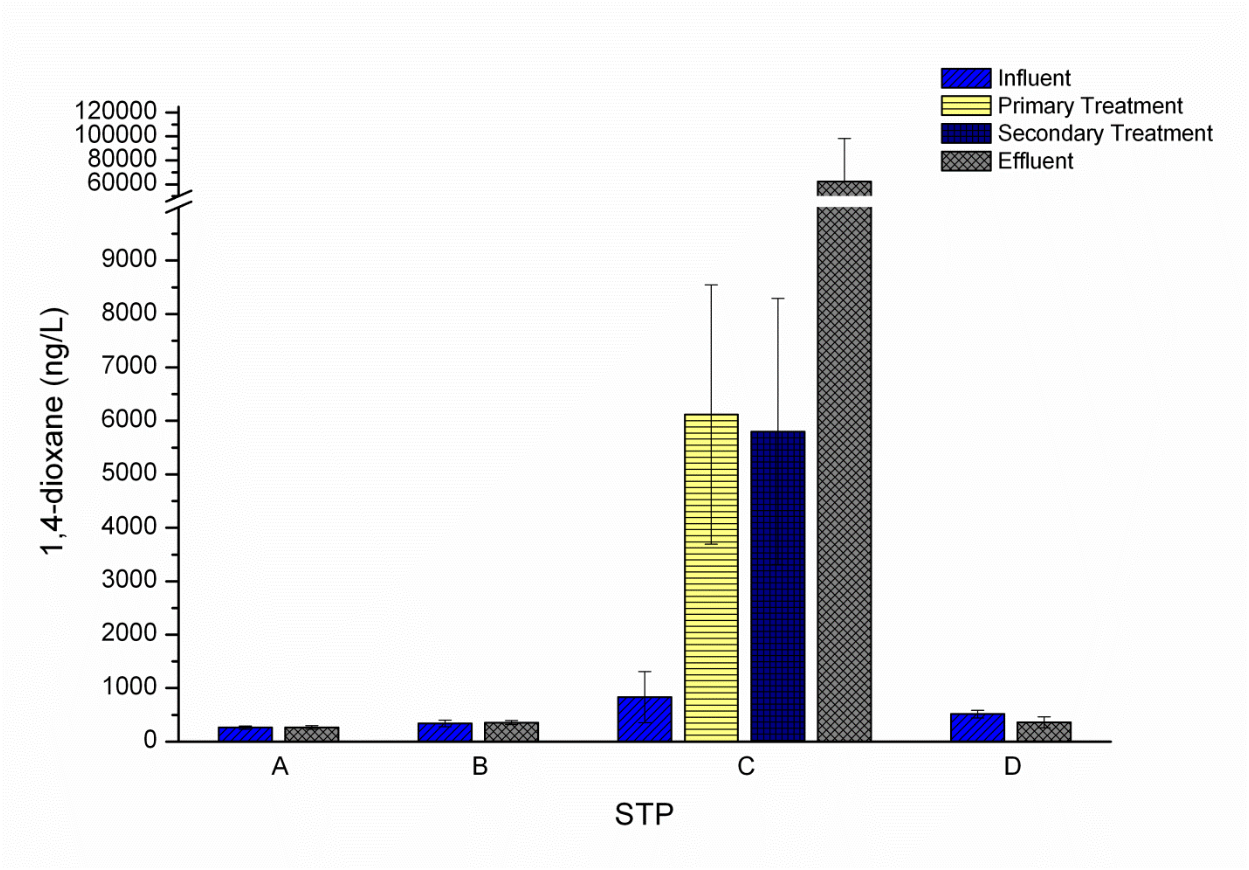


FIGURE 4.2 Average concentration (ng L^{-1}) and a standard deviation of 1,4-dioxane in influent samples, after primary and secondary treatment, and in effluent water samples in four municipal sewage treatment plants (STP) investigated.

According to the company that provided the solvent to STP C, the purity of methanol is between 90 % and 96 %. 100 µL of methanol sample was diluted in 100 mL of ultrapure water and extracted using the SPE method described in Section 4.3.2 to determine the possible 1,4-dioxane impurities in the solvent. As expected, only the methanol samples coming from STP C were positive for 1,4-dioxane. The concentration of 1,4-dioxane differed in the methanol with lot and with a supplier. In the methanol samples from the first supplier 1,4-dioxane ranged between 1,650 µg mL^{-1} to 2,190 µg mL^{-1}. The methanol from the second supplier contained 10 µg mL^{-1} of 1,4-dioxane. The results show that the presence and the amount of 1,4-dioxane as an impurity in methanol is dependent on the supplier and the source of the solvent.

The amount of methanol added to the postanoxic denitrification step depends on the amount of nitrate to be removed and the amount of dissolved oxygen in the influent wastewater to be consumed. At the STP C the solvent is added continuously to the postanoxic denitrification stage. During the two sampling campaigns methanol was added at an average of: 1,860 L d^{-1} during the first sampling period and 2,337 L d^{-1} during the second sampling period. The elevated 1,4-dioxane concentrations in the wastewater after primary and secondary treatment resulted from the redirected sludge dewatering from the postanoxic denitrification step. The methanol samples analyzed from STP C correspond to the methanol used during the second wastewater sampling. Methanol mixing occurs during the methanol delivery and storage, nevertheless one of the methanol samples analyzed makes up the majority of the methanol used during that time. Determined concentration of 1,4-dioxane in that methanol (1650 µg mL^{-1}) was used to calculate the expected concentration and amount (kg d^{-1}) of 1,4-dioxane in the effluent coming entirely from the methanol, assuming that 1,4-dioxane is not used as a carbon source for postanoxic denitrification. For that purpose, the amount of methanol added and the effluent discharge were used. **Table 4.4** lists the amount of methanol added (L d^{-1}), the effluent discharge at the STP C (m^3 d^{-1}), detected amount of 1,4-dioxane in this study (kg d^{-1}), amount of 1,4-dioxane in the effluent calculated based on the amount of the ether detected in the pure methanol sample (kg d^{-1}), and the percent difference between the values. The results show a good agreement between the calculated and measured amounts of 1,4-dioxane in the effluent except for two of samplings on the 01/20/13 and 01/22/13, where the difference was 35.4 % and 44.8 %, respectively. Nevertheless, it can be concluded that the impurity of 1,4-dioxane in the methanol is responsible for the high amount of 1,4-dioxane in the effluent of this sewage treatment plant and corresponds to the amount of the methanol added during the postanoxic denitrification step. The concentration of 1,4-dioxane in the influent, which in the second sampling period was 714 ± 480 ng L^{-1}, has a negligible influence on the concentrations in the effluent. Moreover the results show that methanol from other sources/suppliers does not contain 1,4-dioxane as an impurity.

TABLE 4.4 Amount of methanol (MeOH) used for postanoxic denitrification (in Liters per d) at STP C ,effluent discharge in m^3 d^{-1}, amount of 1,4-dioxane detected (kg d^{-1}) in the effluent in this study, amount of 1,4-dioxane as an impurity (kg d^{-1}) calculated based on the detected concentration in the methanol (1650 µg mL^{-1}) used for denitrification, and percent difference between results.

Sampling Date	MeOH L/d	Discharge m³/d	1,4-dioxane kg/d	1,4-dioxane as impurity kg/d	% Difference
01/17/13	2,608	36,700	3.96	4.30	7.8
01/18/13	2,362	37,900	3.66	3.90	6.1
01/19/13	2,009	36,800	3.56	3.32	-7.4
01/20/13	1,523	59,000	3.40	2.51	-35.4
01/21/13	2,106	67,400	3.37	3.47	2.9
01/22/13	2,383	43,500	2.17	3.93	44.8
01/23/13	3,367	39,000	5.03	5.56	9.5

4.6.2. Temporal and spatial distribution of 1,4-dioxane in surface waters

In order to observe temporal distribution of 1,4-dioxane in the surface water, 24−hour composite samples from the Rhine River were collected for a period of 14 days. **Figure 4.3a** illustrates daily fluctuations of 1,4-dioxane (ng L^{-1}) during the two week profile study at the Rhine Water Control Station Worms, Germany. Detected concentrations of 1,4-dioxane on the left (MWL1) and the right (MWL4) side of the Rhine River are plotted together with the average daily discharge (flow rate in m^3 s^{-1}). The lowest concentration of 1,4-dioxane was detected on the right side of the river and equalled to 250 ng L^{-1}, whereas the highest concentration reached 2,200 ng L^{-1} on the left river side. The average concentration of 1,4-dioxane during the two week profile study was 770 ng L^{-1}. At the MWL1 location (left river side), the quality of the surface water is influenced by the domestic and industrial sewage water predominantly coming from the city of Ludwigshafen, Germany, including 4.5 m^3 s^{-1} treated wastewater from one of Europe's largest chemical industry sites. Several other communal and industrial STP, and the river Neckar have an influence on the Rhine River between km 2 and km 14.9 upstream of MWL4 (right river side). For the period of the first eight days, the concentration of 1,4-dioxane was higher at the MWL1; after that the trend reversed showing slightly higher concentrations of 1,4-dioxane at the MWL4. In general, the concentration of 1,4-dioxane detected increased during the first week of the sampling (08/20/12 – 08/26/12) compared to the following week (08/27/12 – 09/02/12). The discharge of the Rhine River also increased gradually during the sampling. The results suggest the possible entrance of the 1,4-dioxane with both industrial and domestic sewage effluents. The effluents discharged by the communal and/or industrial sewage treatment plants situated nearby most probably had an influence on the extremely high concentration of 1,4-dioxane on 08/24/12 (2,200 ng L^{-1}). Only during the last day of the sampling, the river's discharge reached above average annual discharge of 1,450 m^3 s^{-1}. Therefore, the conditions during the sampling event can be considered as typical for low water levels.

In order to compare the results of the study performed at the Rhine Water Control Station Worms, additionally monthly concentrations of 1,4-dioxane in the Rhine River at the monitoring stations Lobith (km 862) were obtained from the Dutch River Waterworks Association (RIWA-Rijn) in Nieuwegein (Netherlands), where grab water samples collected each month are analyzed for 1,4-dioxane. Based on the results presented in **Figure 4.3a and 4.3b**, it can be concluded that the concentration of 1,4-dioxane in the Rhine River decreases with increasing discharge of the river.

Moreover, it can be assumed that the higher water rate flow dilute the amount of 1,4-dioxane in the surface water. Based on the obtained data from the Rhine Water Control Station Worms, the total loading of the river cannot be exactly calculated. The sampling system for the centre section of the Rhine River − normally fixed to the two bride piers − was out of order due to the bridge's maintenance. The load of organic pollutants is expected to be highest in the middle of the river, because of the higher water flow in this segment (Guedez et al., 2010). Nevertheless, according to the calculations by the Rhine Water Control Station, the sampling site MWL1 and MWL4 represent 10 % and 20 % of the total discharge, respectively (Luckas and Diehl, 2000). Therefore, the average load of 1,4-dioxane on the left side of the river (MWL1) was calculated to equal 16.7 kg d^{-1} and on the right (MWL4) side 5.71 kg d^{-1}. The minimum load was determined in MWL1 (2.32 kg d^{-1}) and the maximum in MWL4 sampling point (35.51 kg d^{-1}).

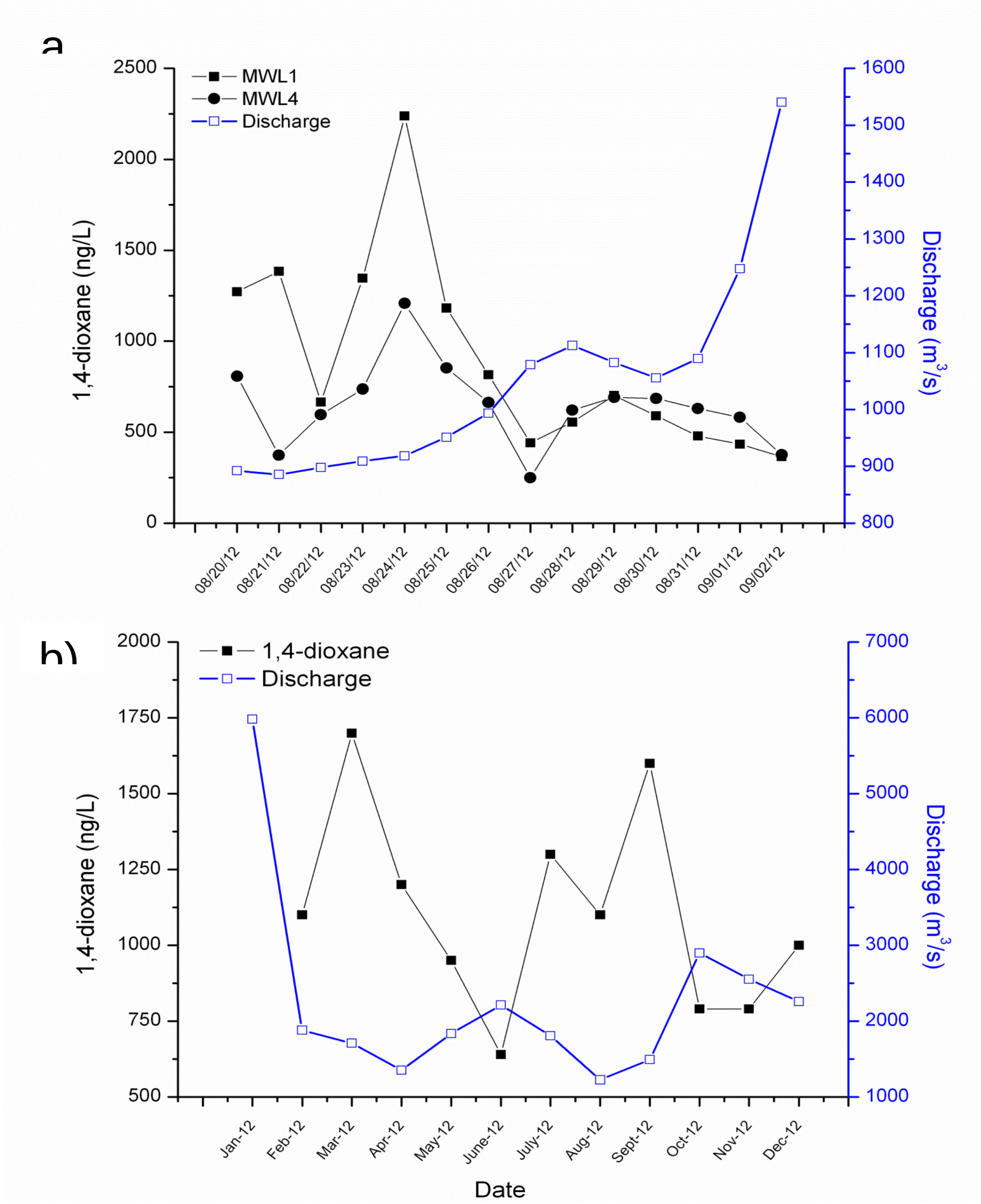


FIGURE 4.3 a) Concentration profile of 1,4-dioxane (ng L^{-1}) on the left (MWL1) and on the right (MWL4) side of the Rhine River during a two week study at the Rhine Water Control Station Worms, Germany with the river discharge values (m^3 s^{-1}). **b)** Monthly concentration of 1,4-dioxane in 2012 at the monitoring station Lobith, Germany with the discharge values. On 11.01.12 concentration of 1,4-dioxane was below detection limit (< 500 ng L^{-1}). (*Source of data shown in Fig.3b*: RIWA-database Nieuwegein)

Furthermore, it can be estimated that approximately 30 % of the total load could be detected, which leads to an overall load of approx. 74.8 kg d^{-1}. The load of 1,4-dioxane is most likely influenced by the discharge of STPs located nearby and fluctuate with time. Based on the data from the Lobith station at the German-Dutch border, the average monthly load of 1,4-dioxane was calculated to be 172 kg d^{-1}, with a minimum of 96.2 kg d^{-1} and a maximum of 251 kg d^{-1}. The average estimated load in Worms is below the minimum load calculated for the Rhine at the Lobith station. The 419 km distance between the two monitoring stations, suggest numerous additional source of 1,4-dioxane entering the Rhine River.

The spatial distribution of 1,4-dioxane in the surface water was studied in three rivers: Oder, Rhine, and Main River. **Table 4.5** summarizes the concentration profile of 1,4-dioxane during the sampling campaigns conducted. The highest average concentration of 664 ng L^{-1} was detected in the Oder River with the minimum of 143 ng L^{-1} and a maximum level of 2,245 ng L^{-1}. Average concentration in the Main River (490 ng L^{-1}) slightly exceeded concentration detected in the Rhine River (470 ng L^{-1}). The maximum concentrations in Rhine and Main Rivers were a little over 850 ng L^{-1}, whereas the minimum levels detected were 210 and 110 ng L^{-1}, respectively.

TABLE 4.5 Summary of 1,4-dioxane concentrations (in ng L^{-1}) in the three rivers investigated.

River	No. of samples	Mean	Median	Max	Min
Oder	49	660	550	2200	140
Rhine	19	470	440	860	210
Main	15	490	530	860	110

In **Figure 4.4**, concentrations of 1,4-dioxane detected at each sampling location are plotted against the distance from the spring of the river. The continuous sampling of the Oder River in August 2012, and the Main and Rhine River show similar patterns, in which 1,4-dioxane concentrations increase with distance.

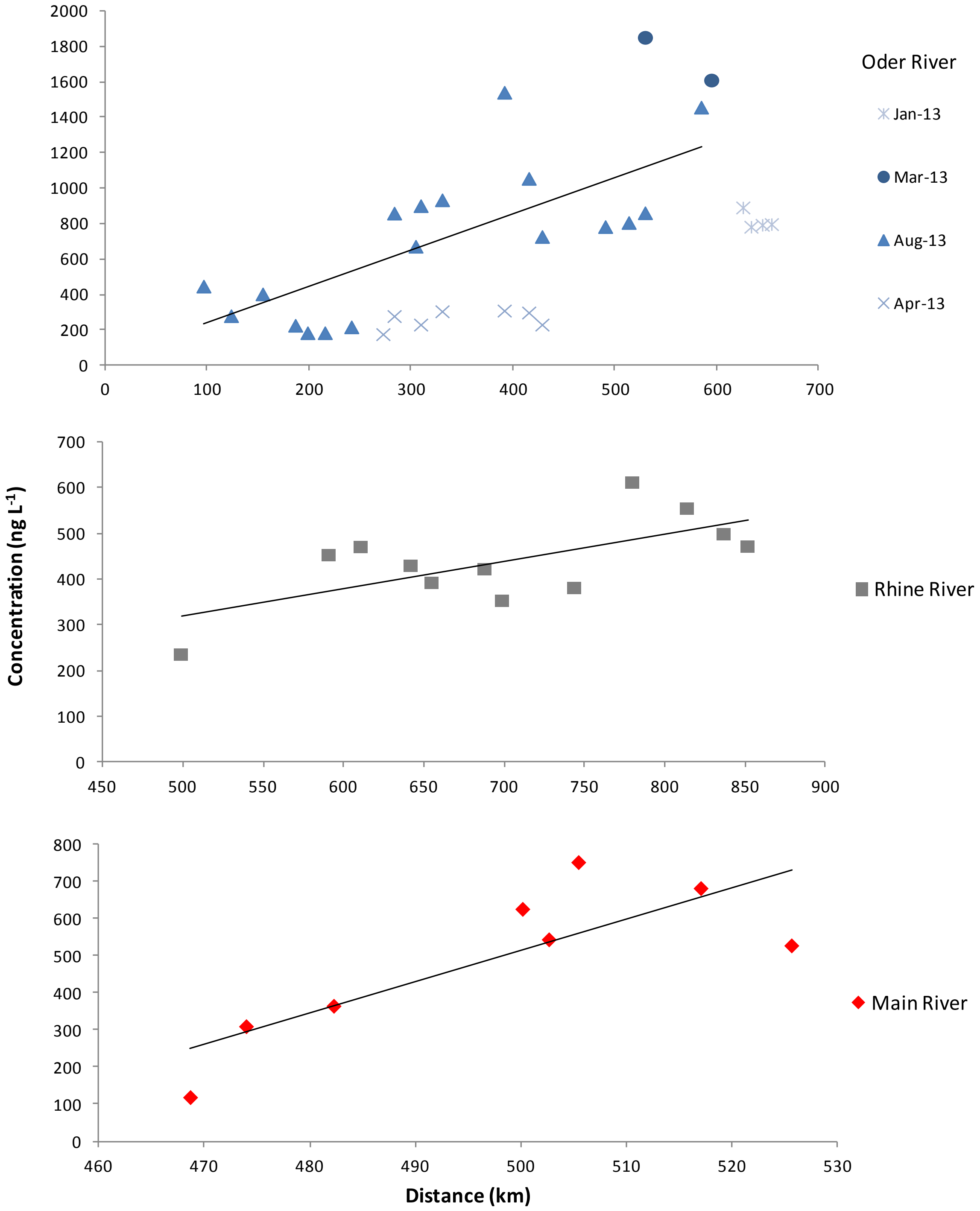


FIGURE 4.4 Spatial distribution of 1,4-dioxane in the Oder, Rhine, and Main River. The trendlines indicate increases in 1,4-dioxane concentration with increasing distance from the spring of the river.

The fluctuations of the concentrations between sampling points is most likely affected by the increasing number of sewage effluent discharging into the river as well as elevation or dilution of concentrations by tributaries. Numerous minor and major tributaries of the Oder, Rhine, and Main River exhibit a high percentage of municipal and industrial wastewater, which can impact the concentration of the receiving waters (**Figure 4.1**). Studies of other trace organic pollutants confirm the plausibility of 1,4-dioxane behaviour in surface water. Sacher et al. (2008) observed the trend of temporal variations of pharmaceuticals and their increasing concentration levels and loads with increasing distance from the spring of the river , but unlike for 1,4-dioxane, no correlation with discharge. Another study focused on the occurrence of perfluorinated surfactants in the surface waters, seven of which were detected in the Rhine River at concentrations below 200 ng L^{-1} (Skutlarek et al., 2006). The location of the main source of pollution was found to exist in the tributaries: Ruhr and Moehne River.

Based on the concentrations determined and flow rate of the river (for sampling points where data on discharge was available: **Table 4.3**), the daily transport of 1,4-dioxane in the surface waters was calculated. **Figure 4.5** illustrates the load of 1,4-dioxane (in kg d^{-1}) in the Rhine, Oder, and Main Rivers. The highest average load of 1,4-dioxane was calculated for the Rhine River (134.5 kg d^{-1}). Taking into consideration the much lower discharge of the Oder River, the average load of 1,4-dioxane was calculated to be 34.1 kg d^{-1}. In the Main River the load, as expected, was the lowest with 6.5 kg d^{-1}. **Figure 4.6** depicts the load of 1,4-dioxane in the Oder River at locations sampled on two different occasions. The results show that the loads of 1,4-dioxane in the Oder River in the samples Od6 and Od7 (both taken in Połęcko, PL) were not constant over time during March and August samplings. Even though the discharge in March was higher (289 m^3 s^{-1}) than in August (97.3 m^3 s^{-1}) the load of 1,4-dioxane was 68.3 kg d^{-1} compared to 7.2 kg d^{-1} in the sample taken during the summer month. Except these two samples, loads of 1,4-dioxane at all other locations sampled on two occasions were similar. In April 2013, when the discharge was almost three times higher than in August 2012, the loads of 1,4-dioxane remained comparable at all sampling points. Therefore, long term temporal variations in the load of 1,4-dioxane occur. Consequently, daily and yearly transport of 1,4-dioxane in the surface water might be under- or overestimated, based on random samplings.

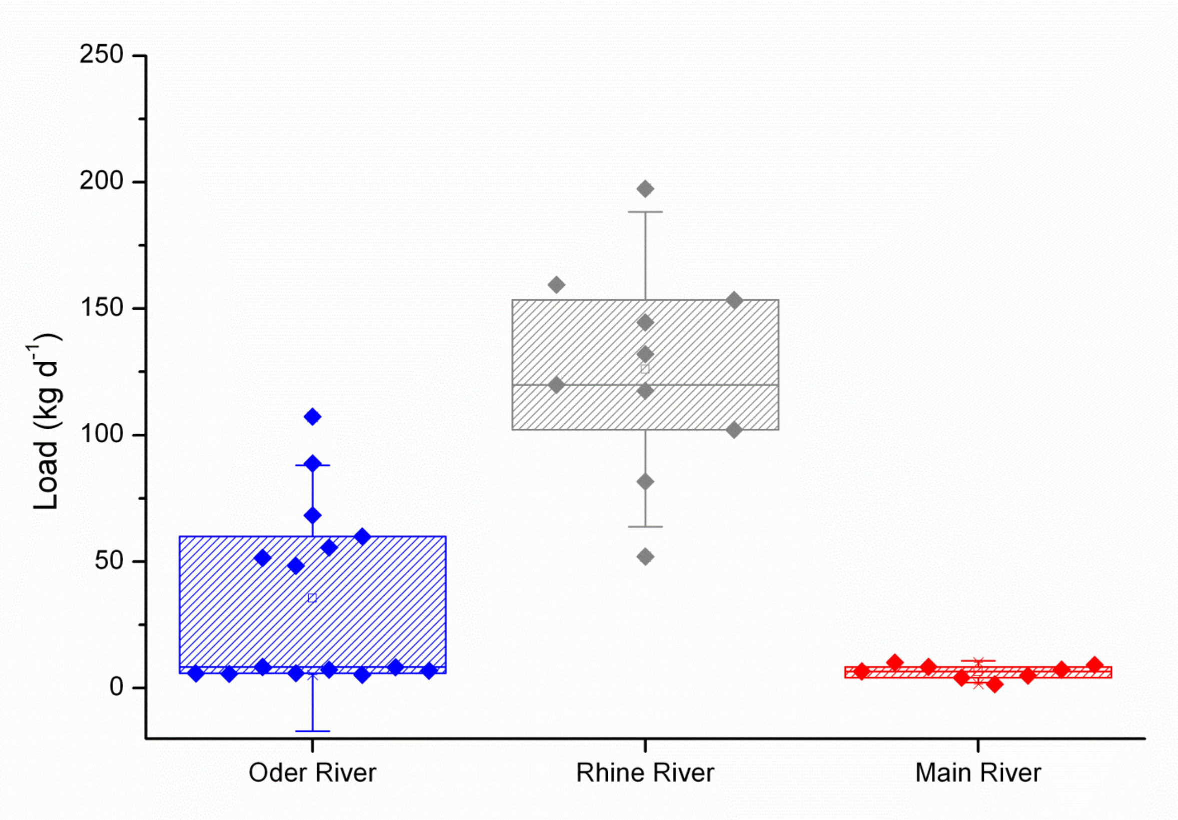


FIGURE 4.5 Load of 1,4-dioxane (kg d^{-1}) in the three rivers sampled. For the Oder and Rhine River load was calculated only at locations, where data on discharge (m^{3} s^{-1}) was available. For the Main River, average discharge of the day (156 m^{3} s^{-1}) was used for 8 locations sampled (~ 50 km of the river). Error bars represent standard deviation.

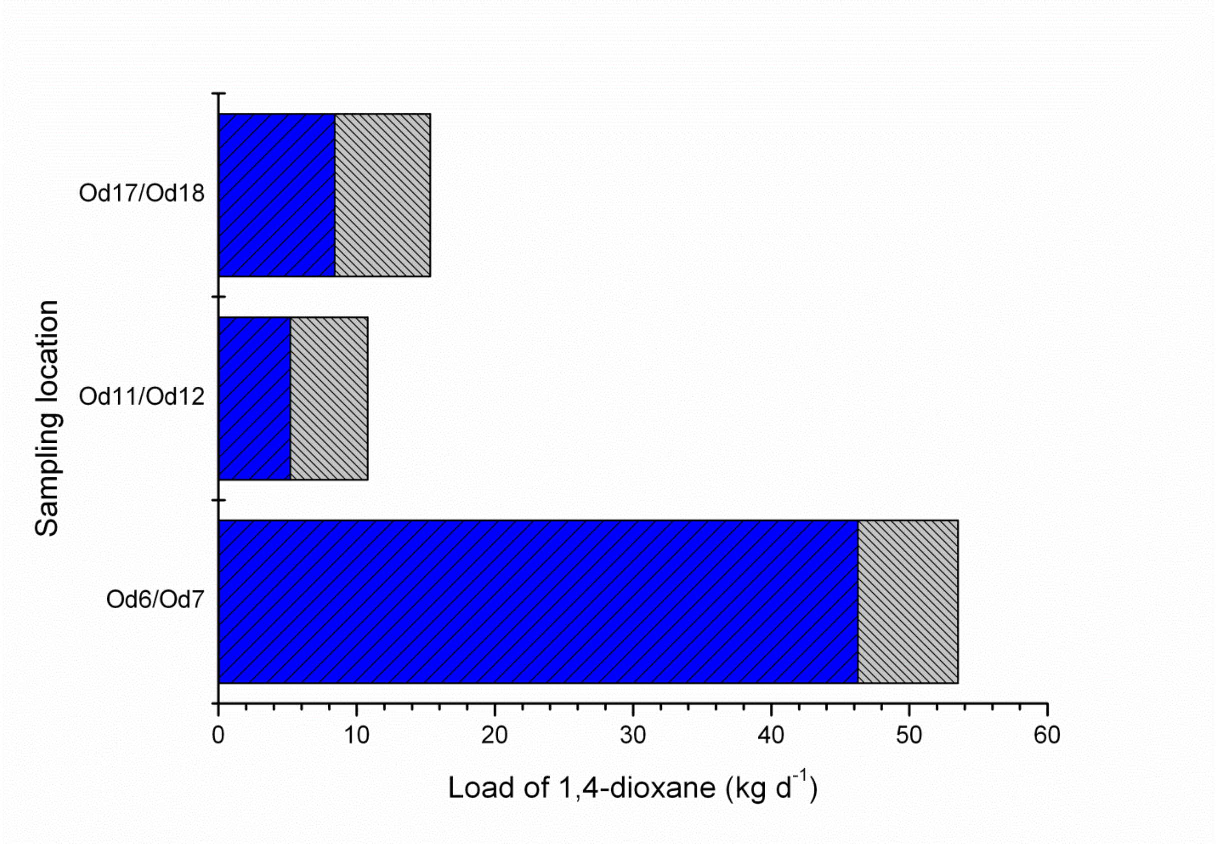


FIGURE 4.6 Loads of 1,4-dioxane (kg d^{-1}) at locations sampled on two different occasions.

Several studies reported the presence of persistent pollutants in the river Rhine and other European waters with which the occurrence of 1,4-dioxane in the Rhine River can be compared. As reported by the Rhine Water Works (RIWA), in its yearly report, the maximum concentration of 1,4-dioxane detected at the Lobith station was 1.7 µg L^{-1} (1700 ng L^{-1}) in 2012 (Rhine Water Works, 2012). In the current study the highest concentration of 2,200 ng L^{-1} was recorded at the Rhine Water Control Station Worms. The water reaching the Lobith station undergoes dilution and a raise in effluent proportion, hence the concentration reported is comparable with the amount reported in this study. According to Loos et al. (2009), many polar organic persistent pollutants in European rivers do not exceed the average concentrations of 250 ng L^{-1}. In that study 1,4-dioxane was not on the list of 35 selected contaminants, although its occurrence and toxicological concerns are comparable with the compounds selected. In the decade long monitoring study, Sacher et al. (2008) reported the occurrence of 12 pharmaceutical residues in the river Rhine. The maximum concentrations of the pharmaceuticals detected did not exceed 900 ng L^{-1}. These studies show that 1,4-dioxane surpasses in concentration many other pollutants found to be significant for the surface water conditions, especially when used for drinking water purposes. The International Association of Waterworks in the Rhine Catchment Area (IAWR) in its memorandum from 2008 has established target limits that apply to surface water used for the production of drinking water (IAWR, 2008). Substances with low biodegradability have been assigned a target value of 1.0 µg L^{-1}. This concentration has been occasionally surpassed in all of the rivers for 1,4-dioxane.

4.6.3. Occurrence of 1,4-dioxane in bank filtration and drinking water

In view of the poor removal of 1,4-dioxane during wastewater treatment and the high concentrations in the surface waters, bank filtration and drinking water samples were investigated for the occurrence of the persistent ether. Samples from two drinking water treatment plants (DWT) were analyzed. **Figure 4.7** illustrates the cross section of the bank filtration area studied, together with the concentration of 1,4-dioxane detected at the DWT 1. In the first sampling well (A) located 20 m from the Rhine River bank, 1,4-dioxane was determined at an average concentration of 570 ng L^{-1} (n = 3) . In the deepest monitoring well the concentration was higher (680 ng L^{-1}) than in the upper and middle wells, although the residence time of water is about twice as high in the bottom well. The infiltrated water in well A and B originates only from the bank filtration. In the well B, 1,4-dioxane was present at an average of 730 ng L^{-1} (n = 3). In well C, the concentration of 1,4-dioxane reached 3,800 ng L^{-1} in the most upper part of the multilevel well, whereas in the two lower wells it was 610 ng L^{-1} (n = 2) on average. The water at this particular well consists of inflowing land groundwater that mixes with bank filtration water only at high surface water levels. Prior to the sampling (10 weeks) the river water levels were between 163 cm and 411 cm. The annual maximum for the year 2012 was 735 cm and the minimum water level was 128 cm. Therefore, the water level prior to and during sampling is not considered as high. Hence, dilution of water in well C is not expected. The groundwater from the land alone was not analyzed for 1,4-dioxane.

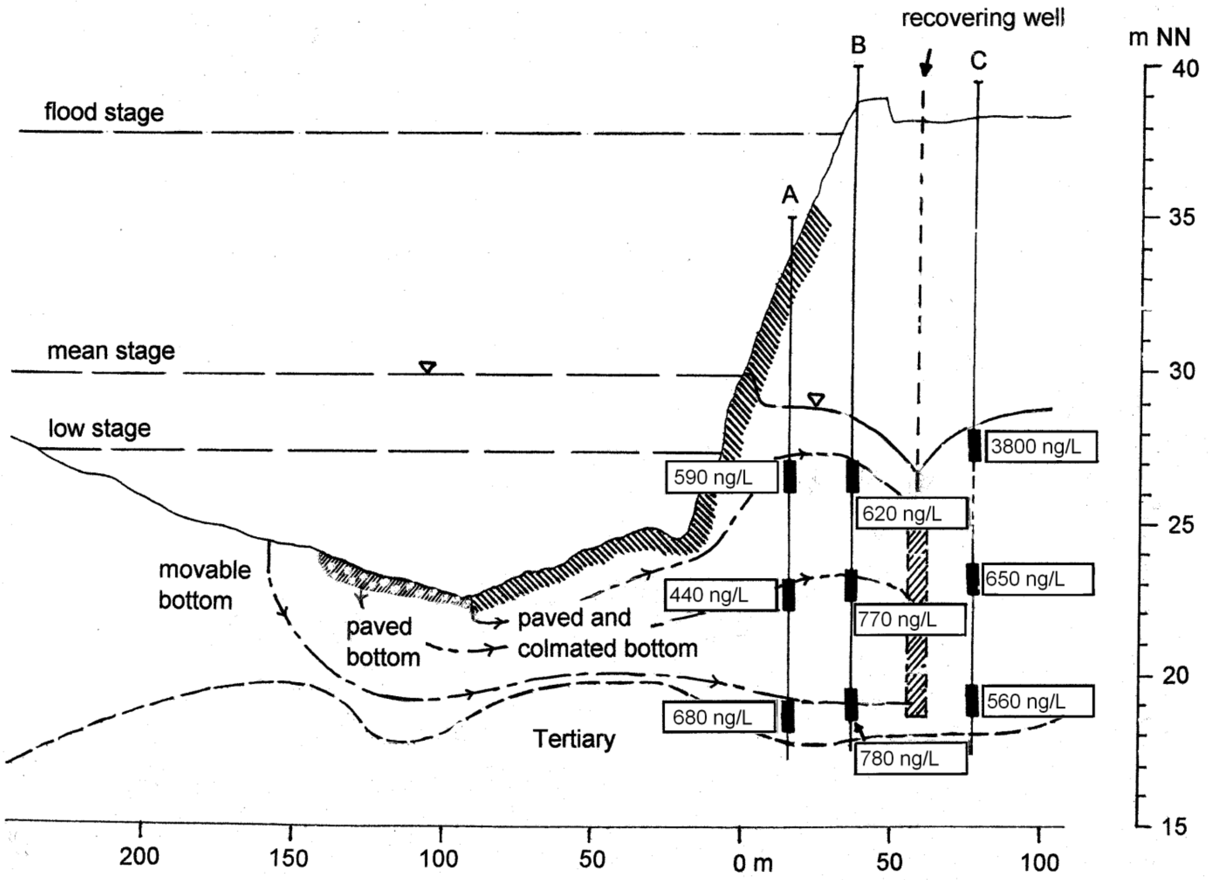


FIGURE 4.7 Hydrological cross section through the Rhine River and the bank filtration site. Concentrations of 1,4-dioxane at multilevel monitoring wells (A-C) are given in a box. Dotted lines indicate the water pathways and flow direction. (*Figure source*: Achten et al., 2002)

The concentrations determined in the Rhine River at the Lobith measuring station can be used to compare the occurrence of 1,4-dioxane during bank filtration at DWT1. In the river water, 1,4-dioxane was present at 790 ng L^{-1} on both 10/17/12 and 11/14/12 (RIWA-database Nieuwegein). Considering the water residence time of 15 – 70 d, the measured concentration in the wells indicates that there was no removal of 1,4-dioxane during bank filtration. Moreover, a significant additional source of 1,4-dioxane from land groundwater is reaching the recovery well causing the high concentration of 3,800 ng L^{-1} in the upper part of well C. The source of the increased 1,4-dioxane concentration in the groundwater needs to be investigated. **Figure 4.8** represent concentrations of 1,4-dioxane in the raw and drinking water samples at two DWT investigated. The raw water at the DWT 1, consisting of 75 % bank filtration water and 25 % groundwater from natural groundwater recharge, contained 670 ng L^{-1} of 1,4-dioxane. Once the water passed through the treatment process (described in Section 3.3) the concentration decreased only to 490 ng L^{-1}. At the DWT 2, the concentration of 1,4-dioxane in the raw water sample (following ozonation, aeration, and gravel filtration) was 650 ng L^{-1}. Once the water passed through another filtration step with activated carbon, the average concentration of 1,4-dioxane dropped to 600 ng L^{-1} (n = 2) in the drinking water. At the same time as the sampling in DWT 2, two Rhine River samples were obtained in which an average concentration of 1,4-dioxane of 770 ng L^{-1} was determined. These results demonstrate that neither bank filtration nor purification of the raw water was capable to remove 1,4-dioxane below detection limit. The reported surface water concentrations do not correspond with the amount of 1,4-dioxane at the time of infiltration, taking into account the residence time of the water during bank filtration. Nevertheless, the concentrations are within the typical range at which 1,4-dioxane has been detected in the Rhine River. As previously discussed, the concentrations of 1,4-dioxane fluctuate in the river water, therefore its presence in the drinking water will also vary.

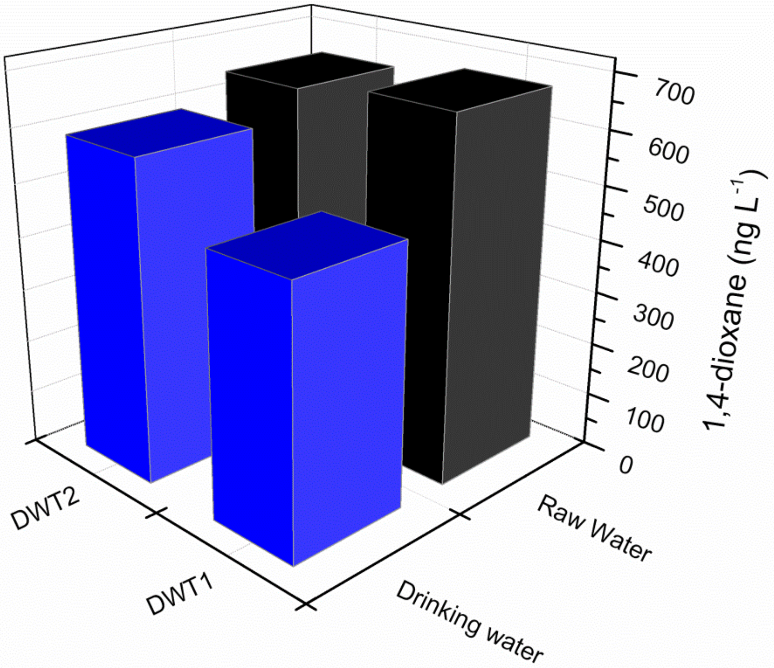


FIGURE 4.8 Concentration of 1,4-dioxane (ng L^{-1}) in the raw water after bank filtration and in the drinking water after water purification.

It is not surprising that concentrations of 1,4-dioxane remained at a high level after bank filtration and drinking water treatment. In a groundwater study at the Oderbruch polder, Germany, 1,4-dioxane showed no attenuation during bank filtration, and the drop in concentration in the groundwater with an estimated age of 42 years was most likely due to lower historical levels in the Oder River (Stepien et al., 2013). Based on the numerous studies conducted, the removal of 1,4-dioxane from water is primarily achieved using advanced oxidation processes (AOP) such as: ozone (O_3)/hydrogen peroxide (H_2O_2); UV/H_2O_2; and Fenton's reagent (Fe and H_2O_2) (Adams et al., 1994; Safarzadeh-Amiri et al., 1997; Mohr, 2010; Suh and Mohseni, 2004; Stefan and Bolton, 1998). These types of processes have not been implemented at the drinking water treatment plants investigated. AOPs represent an alternative drinking water treatment option for substances with relatively low Henry´s constant, high water solubility and low biodegradability. The major drawback of implementing AOPs in water treatment is the cost of necessary devices and the energy requirement. According to the study of Katsoyiannis et al. (2011), O_3/H_2O_2 is an efficient process for organic micropollutants removal and energy requirement is only up to 25 % higher than for ozonation alone. Owing to its strong internal chemical bonding, 1,4-dioxane is commonly considered to be nonbiodegradable. More recent studies demonstrated biodegradation of the cyclic ether by newly isolated bacterial strains such as: *Pseudonocardia* sp. ENV 478 (Vainberg et al., 2006; Masuda et al., 2012); *Mycobacterium* sp PH-06 (Kim et al., 2009); Flavobacterium (Sun et al., 2011). In most cases the presence of the cometabolite tetrahydrofuran was required to observe degradation of 1,4-dioxane in the strain. Moreover, the studies are usually confined to laboratory settings and biodegradation of 1,4-dioxane in samples from the natural environment is not readily reported. Study of Shen et al. (2008) focused on the degradation of 1,4-dioxane under iron-reducing conditions, but amendments were necessary in order to observe significant reduction in the cyclic ether. The physico-chemical properties described earlier ensure that the removal of 1,4-dioxane from environmental samples is difficult, and costly techniques have to be implemented during wastewater, drinking water or groundwater treatment to eliminate efficiently a persistent organic compound such as 1,4-dioxane.

Schriks et al. (2010) established provisional drinking water guideline values for 50 emerging contaminants that are relevant for drinking water and the water cycle. A provisional guideline for 1,4-dioxane based on a specific cancer risk level of 10^{-5} was set at 30 µg L^{-1}. The specific risk level of 10^{-6}, commonly used in the European countries, would result in a provisional guideline value of 3 µg L^{-1} (3000 ng L^{-1}). The author suggested that compounds such as 1,4-dioxane should be regularly monitored in the drinking water, since its guideline value is easily exceeded. The concentrations of 1,4-dioxane detected in the drinking water samples of two DWT plants did not exceed the U.S. EPA regulatory level of 3 µg L^{-1} in the tap water. Nevertheless, the amount of 1,4-dioxane present in the drinking water surpassed the concentration of 350 ng L^{-1}, which as stated by U.S. EPA IRIS, could cause cancer to 1 in 1,000,000 individuals consuming contaminated drinking water. As previously mentioned, the proposed target value for 1,4-dioxane by IAWR in surface waters used in the production of drinking water is 1000 ng L^{-1}, although the German Federal Environmental Agency set a precautionary guidance limit in drinking water for compounds such as 1,4-dioxane to be 100 ng L^{-1}. The concentrations of 1,4-dioxane detected in the drinking water produced by both DWT 1 and 2 exceeded this value four fold. The goal of IAWR is to achieve surface water quality that allows production of drinking water using primarily natural treatment methods. In order to ensure a safe source of drinking water produced from bank filtration, lower regulatory limits should be developed. In view of the fact that 1,4-dioxane cannot be eliminated through natural processes alone, its occurrence in surface waters should be reduced significantly. Industries and sewage treatment plants should intensify their effluent control and reduce surface water pollution with 1,4-dioxane.

4.7 Conclusions

The results of the conducted study confirm the need for 1,4-dioxane monitoring and regulation. The high concentrations of this compound detected in the surface waters and its resistance to natural attenuation pose a threat to drinking water produced through bank filtration. Advanced oxidation processes such as: ozone (O_3)/hydrogen peroxide (H_2O_2); UV/H_2O_2; and Fenton's reagent (Fe and H_2O_2) should be implemented in the water treatment processes to ensure removal of trace organic contaminants such as 1,4-dioxane. Additionally, the search for sources of the 1,4-dioxane in the aquatic environment should be intensified. One source, identified in the present study comes from the contaminated industrial methanol used by one of the STPs as an organic substrate for postanoxic denitrification. STPs should purchase methanol only from companies that certify the absence of 1,4-dioxane and other hardly biodegradable impurities from the supplied product. Further identification of unknown sources of 1,4-dioxane is necessary in order to explain high concentrations found in surface waters. Industries that utilize 1,4-dioxane as a processing solvent should implement vacuum stripping, a process suggested by U.S. EPA, in order to decrease or eliminate the persistent ether from their effluents. Because of possible human carcinogenic properties of 1,4-dioxane, its concentration in wastewater, surface water, and drinking water should be minimized, in order to protect water resources.

Chapter 5 Source identification of high glyme concentrations in the Oder River

5.1. Abstract

The objective of the following study was to identify the source of high concentrations of glycol diethers (diglyme, triglyme, and tetraglyme) in the Oder River. Altogether four sampling campaigns were conducted and over 50 surface samples collected. During the first two samplings of the Oder River in the Oderbruch region (km 626–690), glymes were detected at concentrations reaching 0.065 µg L^{-1} (diglyme), 0.54 µg L^{-1} (triglyme) and 1.7 µg L^{-1} (tetraglyme). The subsequent sampling of the Oder River, from the area close to the source to the Poland–Germany border (about 500 km) helped to identify the possible area of the dominating glyme entry into the river between km 310 and km 331. During that sampling, the maximum concentration of triglyme was 0.46 µg L^{-1} and tetraglyme 2.2 µg L^{-1}; diglyme was not detected. The final sampling focused on the previously identified area of glyme entry, as well as on tributaries of the Oder River. Samples from Czarna Woda stream and Kaczawa River contained even higher concentrations of diglyme, triglyme, and tetraglyme, reaching 5.2 µg L^{-1}, 13 µg L^{-1} and 81 µg L^{-1}, respectively. Finally, three water samples were analyzed from a wastewater treatment plant receiving influents from a Copper Smelter and Refinery; diglyme, triglyme, and tetraglyme were present at a maximum concentration of 1700 µg L^{-1}, 13,000 µg L^{-1}, and 190,000 µg L^{-1}, respectively. Further research helped to identify the source of glymes in the wastewater. The gas desulfurization process Solinox uses a mixture of glymes (Genosorb®1900) as a physical absorption medium to remove sulfur dioxide from off-gases from the power plant. The wastewater generated from the process and from the maintenance of the equipment is initially directed to the wastewater treatment plant where it undergoes mechanical and chemical treatment processes before being discharged to the tributaries of the Oder River. Although monoglyme was also analyzed, it was not detected in any of the water samples.

5.2. Introduction

Glymes (glycol diethers) are polyethylene glycols or polypropylene glycols, end capped with a methyl-, ethyl-, butyl-, or vinyl group. For this study four polyethylene glycols end capped with a methyl group were selected. Monoethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) are widely used industrial solvents. The lack of reactive functional groups makes glymes inert chemically; hence they are often used in chemical synthesis applications. Additionally, their high solvating power and their thermal and chemical stability make them ideal for use as solvents and processing aids in the manufacture and formulation of industrial chemicals. Moreover, their application extends to formulation of paints, inks, cleaning fluids, brake fluids, anti-icing agents etc. (**Table 5.1**). Glymes are also applied as a gas absorption media. Several processes have been developed, such as the Solinox and Selexol, that use a mixture of polyethylene glycol dimethyl ethers [CH3O(CH2CH2O)nCH3; n = 3–9] as a physical solvent to remove sulfur dioxide and/or hydrogen sulfide from flue gases (Clariant, 2013a). The major sources of glyme pollution in surface waters will most likely emerge from their use, manufacturing and processing. According to the European Chemicals Agency (ECHA), numerous glyme suppliers exist in Europe although the actual production volumes are confidential. The European Chemical Substances Information System (ECSIS) lists monoglyme as a low production volume chemical with production and/or import volume of 10–1000 tons per year (ECSIS, 2013). Diglyme is listed by ECSIS as a high production volume chemical, with a production and/or import volume in excess of 1000 tons per year (ECSIS, 2013). According to ECHA, the annual triglyme and tetraglyme import and/or production volume in Europe is between 10 and 100 tons and at above 100 tons per year, respectively (ECHA, 2013).

TABLE 5.1 Physicochemical properties and applications of glymes

IUPAC Name	Common Name	Molecular formula	Boiling point (°C)	Solubility (g/L, at 25 °C)	Henry's law const. (atm×m^3×mol^{-1})	Log P_{ow} [a] (at 25 °C)	Applications [b]
1,2-dimethoxyethane	Monoglyme	$CH_3O(CH_2CH_2O)CH_3$	85	85.2	1.07×10^{-6}	-0.21	Lithium batteries, pharmaceuticals, industrial solvent
bis(2-methoxyethyl) ether	Diglyme	$CH_3O(CH_2CH_2O)_2CH_3$	162	162	5.23×10^{-7}	-0.36	Printing inks, adhesives, pharmaceuticals, sealants, reaction solvent, process chemical
1,2-bis(2-methoxyethoxy)ethan	Triglyme	$CH_3O(CH_2CH_2O)_3CH_3$	216	208.8	4.88×10^{-12}	-0.76	Adhesives, brake fluids, paints, manufacture and formulation of industrial chemicals
Bis[2-(2-methoxyethoxy)ethyl]ether	Tetraglyme	$CH_3O(CH_2CH_2O)_4CH_3$	275	263.9	1.04×10^{-14}	-1.03	Inks, paints, gas absorption liquid, textile, plastics, industrial chemical processes

[a] P_{ow} *n*-octanol water partition coefficient

[b] Source: European Chemicals Agency (ECHA), Clariant, Novolyte

The physicochemical properties of glymes listed in **Table 5.1** indicate that once released into the environment they will persist mainly in the hydrosphere. Glymes are highly soluble in water; they have low octanol–water partition coefficients ($\log P_{ow}$) and also low Henry's law constant, which induce their partition to water, rather than evaporation from water into the gas phase. Hydrolysis is not expected to be an important environmental fate process since these compounds lack functional groups that hydrolyze under environmental conditions. The low logPow values show that glymes are not likely to sorb to soil and have a low bioaccumulation potential.

The rising concern about the use, exposure, and a possible environmental contamination with glycol diethers is reflected in their reproductive toxicity (US EPA, 2011). Monoglyme, diglyme and triglyme have been shown to cause reproductive and developmental effects in experimental animals (Hardin, 1983; George et al., 1987; Schwetz et al., 1992; ECETOC, 2005). Human exposure to these glymes may also cause infertility and harm to an unborn child (US EPA, 2011). Moreover, destruction of red blood cells and the blood forming organs may follow (ECETOC, 2005). Results of metabolic studies suggest that 2-methoxyacetic acid, a product of glyme metabolism, is responsible for their toxicity (WHO, 2002). Supposedly, the presence of longer alkyl groups at the glyme terminal ends and more ethylene glycol groups in the middle of the glyme molecule both act to reduce their toxicity (ECETOC, 2005). According to the data provided by the European Chemicals Agency, the predicted no-effect concentration (PNEC) in the freshwater for three glymes was derived to be 6400 $\mu g\ L^{-1}$ (ECHA, 2013). Moreover, the oral derived no-effect level (DNEL) for general population is 0.23 mg/kg bw/day, 1.04 mg/kg bw/day, and 3.13 mg/kg bw/day for monoglyme, diglyme, and triglyme, respectively (ECHA, 2013).

Recently, the US Environmental Protection Agency presented a "Significant New Use Rule" for 14 glymes that are in use in the United States (US EPA, 2011). The purpose of the document is to control and limit a significant new use of these glymes by manufacturers and users, but it does not create restrictions for previously registered applications of these solvents. Also in Europe, numerous regulations are in place that limit the use of glymes found toxic for reproduction. Annex XV, Group 30 of the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) confine the presence of monoglyme, diglyme, and triglyme to a generic concentration of 0.3% to be present on the market as a substance, constituent of a substance or in mixtures (ECHA, 2011a,b,c). Additionally, Directive 2009/48/EC restricts the use of these glymes in toys or in components of toys, and the Cosmetic Directive 76/768/EEC limits the use of glymes as a composition of cosmetic products. Moreover, the

Directive 2004/42/EC places a limitation of emission of volatile organic compounds (boiling point < 250 °C) used as organic solvents in certain paints and varnishes (ECHA, 2011a,b,c).

Little information is available on the historical and current concentrations of glymes in surface waters. In the Netherlands, diglyme, triglyme, and tetraglyme were identified during a wide-range screening of micro-contaminants in Dutch rivers, with concentrations reaching 1 µg L−1 (van Steel et al., 2002). In 2005, high concentrations of diglyme (max. 5.60 µg L^{-1}), triglyme (max. 2.95 µg L^{-1}), and tetraglyme (max. 1.45 µg L^{-1}) were reported in the river Rhine (RIWA, 2005). The RIWA (2006) report states that the high glyme concentrations in the Rhine River emerged from effluents of an industrial wastewater treatment plant located in Wiesbaden, Germany, but the industry responsible for the pollution was not identified. Consequently, a guideline value has been set during the Donau-, Mass-, and Rhine Memorandum in 2008, which limits the presence of individual glymes and other trace organic compounds to 1.0 µg L^{-1}(Wirtz, 2009). Moreover, the objective of the memorandum was to protect drinking water produced using the River Rhine from persistent organic compounds (such as glymes), which are not easily removed during water treatment. According to a current report on the Rhine River glymes are no longer present in the river above detection limits (RIWA, 2012).

The purpose of the present study was to determine the occurrence of diglyme, triglyme, and tetraglyme in the Oder River and to identify their possible pollution sources. Besides the above mentioned report from the Rhine River, possible sources of glymes in the surface waters have not been identified and reported before.

5.3. Materials and methods

5.3.1. Chemicals and reagents

Monoglyme (99%), 4-chlorotetrahydropyran (96%), and 1,4-dioxane-d_8 (99%) were purchased from Sigma–Aldrich (Steinheim, Germany). 4−Chlorotetrahydropyran was used as an internal standard (IS) and 1,4-dioxane-d_8 as a surrogate (SU). Diglyme was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Triglyme (99.8%) and tetraglyme (98%) were acquired from Alfa Aesar (Karlsruhe, Germany) and Fluka (Steinheim, Germany), respectively. Analytical grade dichloromethane (DCM), which was distilled before use, and hypergrade methanol, used for extraction and standard preparation were purchased from Merck (Darmstadt, Germany). An Astacus water purification system from MembraPure (Bodenheim, Germany) was utilized in order to produce ultrapure water for determination of method blanks and spike preparation.

Sodium bisulfate was obtained from Aldrich Chemistry (Steinheim, Germany) and was used as received. Anhydrous sodium sulfate was purchased from Sigma Aldrich (Seelze, Germany) and conditioned at 400 °C for 4 h before use. Individual and composite stock solutions (1 μg μL^{-1}) of glymes, SU, and IS were prepared in methanol. Subsequent working standards were obtained through appropriate dilutions of stock solutions in DCM. The standards were stored in the dark at 5 °C and replaced on monthly basis.

5.3.2. Analytical methods

Solid phase extraction (SPE) method was used for an enrichment of monoglyme, diglyme, triglyme, and tetraglyme from aqueous samples. Either a 100 mL or a 500 mL sample volume was loaded onto a Supelclean™ ENVI-CarbTM Plus (Supelco, bed wt. 400 mg, 1 mL) and “Resprep® activated coconut charcoal SPE cartridges” (Restek, 80–120 mesh, approximately 150 μm, 2 g, 6 mL), respectively. The cartridges obtained from Supelco were used during the last two sampling campaigns due to a similar performance at lower cost compared to the Resprep® cartridges. The aqueous samples obtained from the wastewater treatment plant were subjected to a pressure filtration before extraction to prevent cartridges from clogging. Surface water samples did not require filtering. A stainless steel pressure holder (2.12 L; Sartorius, Goettingen, Germany) equipped with a 142 mm diameter borosilicate glass fiber filter (Filter pore size <1 μm; type A/E, Pall, Dreieich, Germany) was used for sample filtration. The filters were sonicated in DCM and heated to 400 °C for 2 h before use. After each blank, spike, and sample filtration the apparatus was thoroughly cleaned with ultrapure water. The SPE method utilizing Resprep® cartridges for glyme extraction was previously described in detail by Stepien and Püttmann (2013). The extraction with “Supelclean™ ENVI-CarbTM Plus” cartridges required a smaller volume of both water sample (100 mL) and the elution solvent (2 mL). One mL of DCM and 2 mL of each methanol and ultrapure water were necessary for the conditioning of the cartridges prior to the sample loading. After the aqueous sample passed through the cartridges, the material was first washed with 2 mL of 20% methanol solution. Thereafter, analytes of interest were eluted with 2 mL DCM. Subsequently, the extracts were passed through a sodium sulfate column in order to remove water from the solvent. Five hundred μL of an extract was spiked with 10 μL of IS (0.125 μg μL^{-1}) and placed in the autosampler for GC/MS analysis. All samples were analyzed using Thermo Finnigan Voyager GC/MS with Trace 2000 GC (ThermoQuest Finnigan, Dreieich, Germany), equipped with a DB−624 capillary column (30 m length, 0.25 mm ID, 1.4 μm film thickness) (Agilent, Waldbronn, Germany). The instrument conditions and quantitation method have been previously described in Stepien and

Püttmann (2013). XCalibur software (Thermo Fisher Scientific, version 2.0.7) was used for data processing.

5.3.3. Quality assurance

Amber glass bottles used for sample collection were pre-cleaned with distilled water and methanol and subsequently heated in the oven at 110 °C for a minimum of 2 h. Sodium bisulfate was added as a preservative to each bottle at 1 g per liter. Following collection, the water samples were stored in refrigerators during transport at a temperature below 10 °C. Before extraction and analysis, samples were stored in a refrigerated storage room at 4 °C for a maximum of seven days. With each batch of 17 samples, a blank and control standards were extracted. Each water sample and quality control standard was enriched with 5 μL of a surrogate (1.0 or 0.20 $\mu g\ \mu L^{-1}$) to reach the final concentration of 10.0 $\mu g\ L^{-1}$ in the extract. Control standards were spiked close to the method detection limit or mid-point of the calibration curve. The acceptable recovery for a surrogate and a spike was ±30%. The calibration curve ranged from 0.040 $\mu g\ L^{-1}$ to 5.0 $\mu g\ L^{-1}$. The limits of quantitation (LOQ) for monoglyme, diglyme, triglyme, and tetraglyme were determined for each SPE cartridge in ultrapure water and surface water. The method utilizing Resprep® coconut charcoal cartridges and 500 mL of a sample gave the following LOQs for monoglyme, diglyme, triglyme, and tetraglyme: 0.024 $\mu g\ L^{-1}$, 0.047 $\mu g\ L^{-1}$, 0.055 $\mu g\ L^{-1}$, 0.057 $\mu g\ L^{-1}$ in ultrapure water and 0.032 $\mu g\ L^{-1}$, 0.044 $\mu g\ L^{-1}$, 0.035 $\mu g\ L^{-1}$, 0.041 $\mu g\ L^{-1}$ in surface water, respectively (Stepien and Püttmann, 2013). The method using Supelclean™ ENVI-CarbTM Plus cartridges gave a LOQ of 0.030 $\mu g\ L^{-1}$ for monoglyme, 0.067 $\mu g\ L^{-1}$ for diglyme, 0.069 $\mu g\ L^{-1}$ for triglyme and 0.067 $\mu g\ L^{-1}$for tetraglyme in ultrapure water. In the surface water, the LOQ for monoglyme, diglyme, triglyme and tetraglyme was calculated to be 0.035 $\mu g\ L^{-1}$, 0.032 $\mu g\ L^{-1}$, 0.044 $\mu g\ L^{-1}$, and 0.047 $\mu g\ L^{-1}$, respectively.

5.4. Site description and sampling methods

5.4.1. Description of the study area

Oder River is the second longest river in Poland with 854 km length and a total watershed area of 118,861 square kilometers, of which almost 90% is on the Polish territory. The river rises in the Oder Mountains in the Czech Republic, flows through western Poland, later creating a 187 km border between Poland and Germany. The flow of the river is mainly in the southwestnorthwest direction, but it changes to the northward trend as it nears the Baltic Sea. Numerous tributaries enter the Oder River, which have a profound influence on the river's condition. Additionally, numerous industries located close to the river are responsible for severe pollution; such industries include steelwork, metal processing, electrical industry, printing industry, paper and wood factory, chemical industry, etc. Two periods of high water levels occur in the Oder catchment. Winter floods happen usually in February and March due to snow melt and summer floods in August due to high precipitation (Mudelsee et al., 2003). Kaczawa River is a left tributary of the Oder River and it discharges north of the city of Ścinawa. The river is 83.9 km in length with a catchment area of 2261 km^2. The Kaczawa River is used in the production of a drinking water for the city of Legnica, which is being collected 32 km before it discharges into the Oder River. Czarna Woda is a left tributary of Kaczawa River and discharges to Kaczawa River 22.2 km before it reaches the Oder River. Czarna Woda stream is 48.0 km long with a 985 km^2 catchment area.

5.4.2. Surface water sampling

Based on the previously reported high concentrations of glymes in the Oder River by Stepien and Püttmann (2013), subsequent investigations were carried out between May 2012 and April 2013. A total of fifty samples (n = 50) were collected from the Oder River. In **Fig. 5.1** the study area and the sample IDs of the Oder River samplings are shown. During the last major sampling campaign of the Oder catchment, two samples were obtained from both the Kaczawa River and the Czarna Woda stream. Manually collected grab samples were taken from the bridge, shore line, or ship where possible. In numerous locations samples from both sides of the river were gathered in order to facilitate identification of a possible glyme entry . Amber glass bottles containing sodium bisulfate as a preservative were filled to the top, leaving no headspace. Samples were kept cooled during transport. **Table 5.2** lists the locations, date, and conditions during surface water samplings.

TABLE 5.2 Locations, date, and conditions during surface water sampling.

Sample ID	River sampled	River km	Sampling Location	River Side	Level (cm)	Discharge ($m^3 s^{-1}$)	Sampling date
OD−1	Oder	97	Koźle	R, L	276		08/31/12
OD−2	Oder	124	Krapkowice	R, L	217		08/31/12
OD−3	Oder	155	Opole	R	405		08/31/12
OD−4	Oder	187	Kopanie	L			08/30/12
OD−5	Oder	199	Brzeg	R, L	126		08/30/12
OD−6	Oder	216	Oława	R, L	177		08/30/12
OD−7	Oder	242	Wrocław	L	314		09/01/12
OD−8	Oder	272	Uraz	R			04/10/13
OD−9	Oder	284	Brzed Dolny	R	196	124	08/30/12
OD−10	Oder	284	Brzed Dolny	R			04/10/13
OD−11	Oder	305	Malczyce	L			08/30/12
OD−12	Oder	310	Kawice	R, L			08/30/12
OD−13	Oder	310	Kawice	R, L	354	291	04/10/13
OD−14	Oder	331	Ścinawa	R, L	151	104	08/30/12
OD−15	Oder	331	Ścinawa	R, L	295	263	04/09/13
OD−16	Oder	392	Glogów	R, L	157		08/30/12
OD−17	Oder	392	Glogów	R, L			04/09/13
OD−18	Oder	416	Bytom Odrzański	L			08/30/12
OD−19	Oder	416	Bytom Odrzański	L			04/09/13
OD−20	Oder	429	Nowa Sól	R, L	142	82	08/30/12
OD−21	Oder	429	Nowa Sól	R, L	307	283	04/09/13
OD−22	Oder	491	Brody	R, L	142	87	08/29/12
OD−23	Oder	514	Krosno Odrzańskie	R			08/29/12
OD−24	Oder	530	Połęcko	R	77	97	08/29/12
OD−25	Oder	585	Słubice	R			08/29/12
OD−26	Oder	585	Frankfurt	L	141		08/29/12
OD−27	Oder	626	Genschmar	L			01/31/12
OD−28	Oder	634	Groß-Neuendorf	L			01/31/12
OD−29	Oder	645	Güstebieser Loose	L	285	362	05/23/12
OD−30	Oder	645	Güstebieser Loose	L	436	806	01/31/12
OD−31	Oder	654	Bienenwerder	L	436	806	01/31/12
OD−32	Oder	654	Bienenwerder	L	287	377	05/24/12
OD−33	Oder	661	Cedynia	R	289		05/23/12
OD−34	Oder	662	Hohenwutzen	L	289	381	05/23/12
OD−35	Oder	665	Hohensaaten	L	289	381	05/23/12
OD−36	Oder	672	Bielinek	R	301		05/23/12
OD−37	Oder	690	Krajnik Dolny	R	581		05/23/12
CW−1	Czarna Woda		Reszotary		160		04/10/13
CW−2	Czarna Woda		Legnica				04/10/13
KW−1	Kaczawa		Legnica		199	18	04/10/13
KW−2	Kaczawa		Prochowice				04/10/13

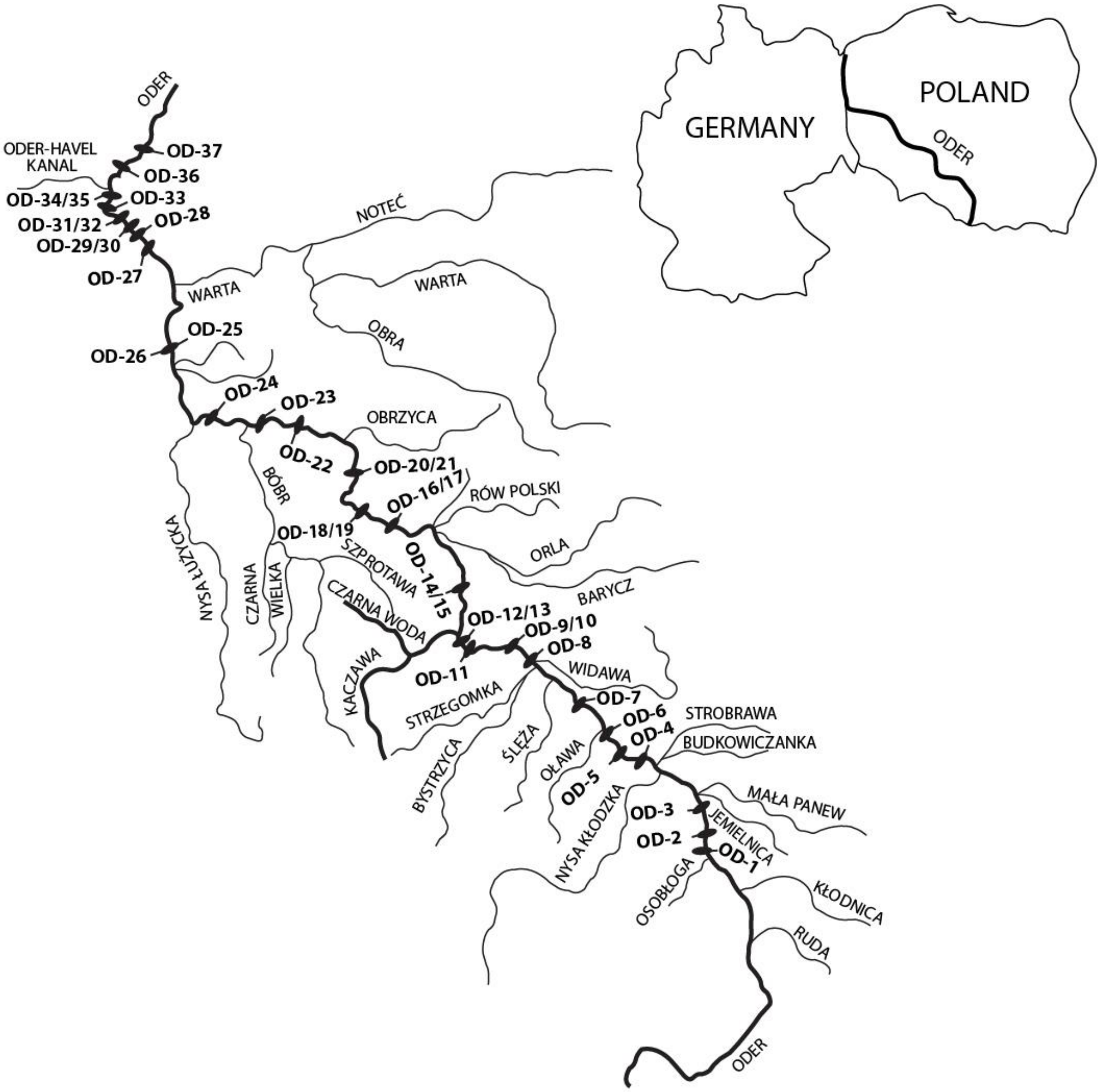


FIGURE 5.1 Map of sampling points along the Oder River with sample IDs.

5.4.3. Wastewater sampling

Manually collected grab samples were obtained from three unidentified unit operations in the wastewater treatment plant (WWTP) located close to the city of Legnica. The plant has a capacity of 22,400 $m^3 d^{-1}$ and treats mainly water originating from the copper industry located in the area. About 1,4 million cubic meters of wastewater are treated annually. Mechanical and chemical treatment processes such as flocculation, coagulation, and sedimentation are employed before the water is discharged to the receiving surface water. The wastewater does not undergo any biological treatment steps. Details about the wastewater treatment plant were not made available due its privacy policies.

5.5. Results and discussion

5.5.1. Occurrence of glymes in the Oder River

The extensive samplings of the Oder River helped to observe the occurrence of glymes in the river course (**Fig. 5.1**) and to determine their point of entry. In order to facilitate determination of the possible entry locations of glymes, samples from the right and left sides of the river were collected. By implementing this technique one is also able to determine whether the contamination might be coming from one of the tributaries of the river. Initially, samples from the river at the border of Poland and Germany (from km 626 to km 690) were taken in January (n = 4) and May (n = 7) 2012. These samplings were meant to determine if glymes are present in the Oder River and establish their possible sources. In August 2012, about 500 km of the Oder River was investigated in order to locate their possible point of entry (n = 28). Once the area of heavy pollution with glymes was identified between km 310 and km 331, further analysis (n = 11) of the river was conducted in April 2013 focusing on this section, where previously the highest concentrations were detected. **Table 5.3** presents the average concentrations of each glyme detected, with minimum and maximum concentrations observed.

TABLE 5.3 Average, minimum and maximum concentrations of diglyme, triglyme, and tetraglyme, in µg L^{-1}, on the left and right riverbank, during four sampling campaigns.

Sampling campaign	**No. of samples**	**Mean/Min/Max**	**Diglyme (µg L^{-1})**	**Triglyme (µg L^{-1})**	**Tetraglyme (µg L^{-1})**
January, 2012	4	Mean −Left	0.07	0.49	1.61
	4	Min	0.05	0.21	1.47
	4	Max	0.07	0.54	1.73
May, 2012	3	Mean − Right	0.03	0.06	0.33
	4	Mean − Left	0.07	0.17	1.05
	7	Min	0.03	0.05	0.26
	7	Max	0.07	0.20	1.39
August, 2012	14	Mean − Right	n.d.	0.15	0.34
	14	Mean − Left	n.d.	0.22	0.61
	28	Min	n.d.	0.07	0.03
	28	Max	n.d.	0.46	2.21
April, 2013	6	Mean − Right	0.06	0.47	7.87
	5	Mean − Left	0.06	0.70	14.73
	11	Min	0.06	0.25	0.08
	11	Max	0.06	1.01	28.53

n.d. - not detected

The first sampling campaign in the Oderbruch area showed that diglyme, triglyme and tetraglyme are present in the Oder River at maximum concentrations of 0.065 µg L^{-1}, 0.49 µg L^{-1}, and 1.6 µg L^{-1}, respectively (**Table 5.3**). Results of the subsequent sampling presented that the glyme concentration is greater on the left side of the river (**Table 5.3**), suggesting Lusatian Neisse (Nysa Łużycka), a left tributary of the Oder River, as a possible source of contamination. Water samples taken from Lusatian Neisse however, contained no glymes. One possible explanation for this discrepancy is the presence of a minor source of glymes entering on the left side downstream of the Lusatian Neisse tributary. Hence, the objective of the next sampling campaign was to determine the area or areas where glymes are discharged into the Oder River. Water samples from almost 500 km of the river were collected starting close to the Oder source.

Fig. 5.2 illustrates the concentrations of triglyme and tetraglyme during sampling campaigns of the Oder River done in August 2012 and in April 2013. During the August 2012 sampling diglyme was not detected and in April 2013 it was detected only in one location (OD-15, km 331, n = 2) with a maximum concentration of 0.057 µg L^{-1} (**Table 5.3**). Based on the results from all sampling campaigns, diglyme occurs in the Oder River mainly below or close to the detection limit of the method. In August 2012, triglyme was first detected in the OD-14 sampling location (km 331) with a concentration of 0.46 μg L^{-1} on the left river bank exceeding twofold the concentration detected on the right bank of the Oder River. Its presence decreased fourfold on both sides of the river at the last sampling collection points (OD−25 and OD−26). This drop in the concentrations is most likely a result of a dilution of the compound in the surface water, since these sampling points are located in the Oder-Neisse line. Tetraglyme was present in the samples located closest to the source of the river (OD−1 and OD−2, km 217 and 276, respectively) at concentrations ranging between 0.11 μg L^{-1} and 0.61 μg L^{-1}. According to the information on the European Chemicals Agency website, tetraglyme is produced in this area by one chemical production company (ECHA, 2013). Dilution of the concentration to slightly above detection limit was observed until the sampling point OD−14 (km 331), where the concentration of tetraglyme increased again to 0.58 μg L^{-1} on the right river bank and 1.2 μg L^{-1} on the left river bank. From then on, the amount of tetraglyme increased with distance until OD−20 (km 429), where it reached 2.2 μg L^{-1} on the left bank and 1.7 μg L^{-1} on the right bank of the river. In samples OD−22 to OD−26 (km 491 and km 585), the concentrations were much lower with a maximum of 0.33 μg L^{-1}. At these locations samples were taken on 08/29/12, whereas sampling closer to the source was done a day later, which might explain the variation. Moreover, at these locations, the Oder River is joined by its numerous major tributaries such as Bóbr and Lusatian Neisse, which also might cause a dilution of the concentrations. During this sampling it was determined that both triglyme and tetraglyme were present on the left bank at concentrations higher than that of the right bank. This suggests that the pollution is coming either from a tributary, or from a municipal/industrial sewage treatment plant located on the left side of the river. Moreover, both compounds showed up at increased concentrations at the location OD−14 (km 331), suggesting that a source of the glyme pollution is located upstream from this area. Therefore, the focus of the last sampling in April 2013 was mainly the area between km 310 and km 429. At that time, triglyme was detected in the Oder River at much higher concentrations reaching over 1.0 μg L^{-1} and the concentration increased with distance over the sampling area investigated (OD−15, km 331 to OD−21, km 429). Tetraglyme was present again at low concentrations between the river km 272 and km 310 (about 0.10 μg L^{-1}) verifying that the predominant source is not located in that area. The amount of tetraglyme in the river increased with distance between OD−15 (km 331) and OD−21 (km 429), reaching a maximum of 29 μg L^{-1} on the right river bank at OD−21. Further sampling locations were not investigated during this sampling campaign. The increasing trend in the concentration of both compounds during this campaign might be explained by the sampling trend and the discharging source. The samples were collected in an upstream direction with OD-21 sampled first and OD-15 sampled at the end of the day. Moreover, the discharge of glymes into the surface water might have occurred recently with peak concentrations detected at OD−21. As previously mentioned, the predicted no-effect concentration for diglyme and triglyme is 6400 μg L^{-1}. This level has not been exceeded for any of the glymes in the samples collected.

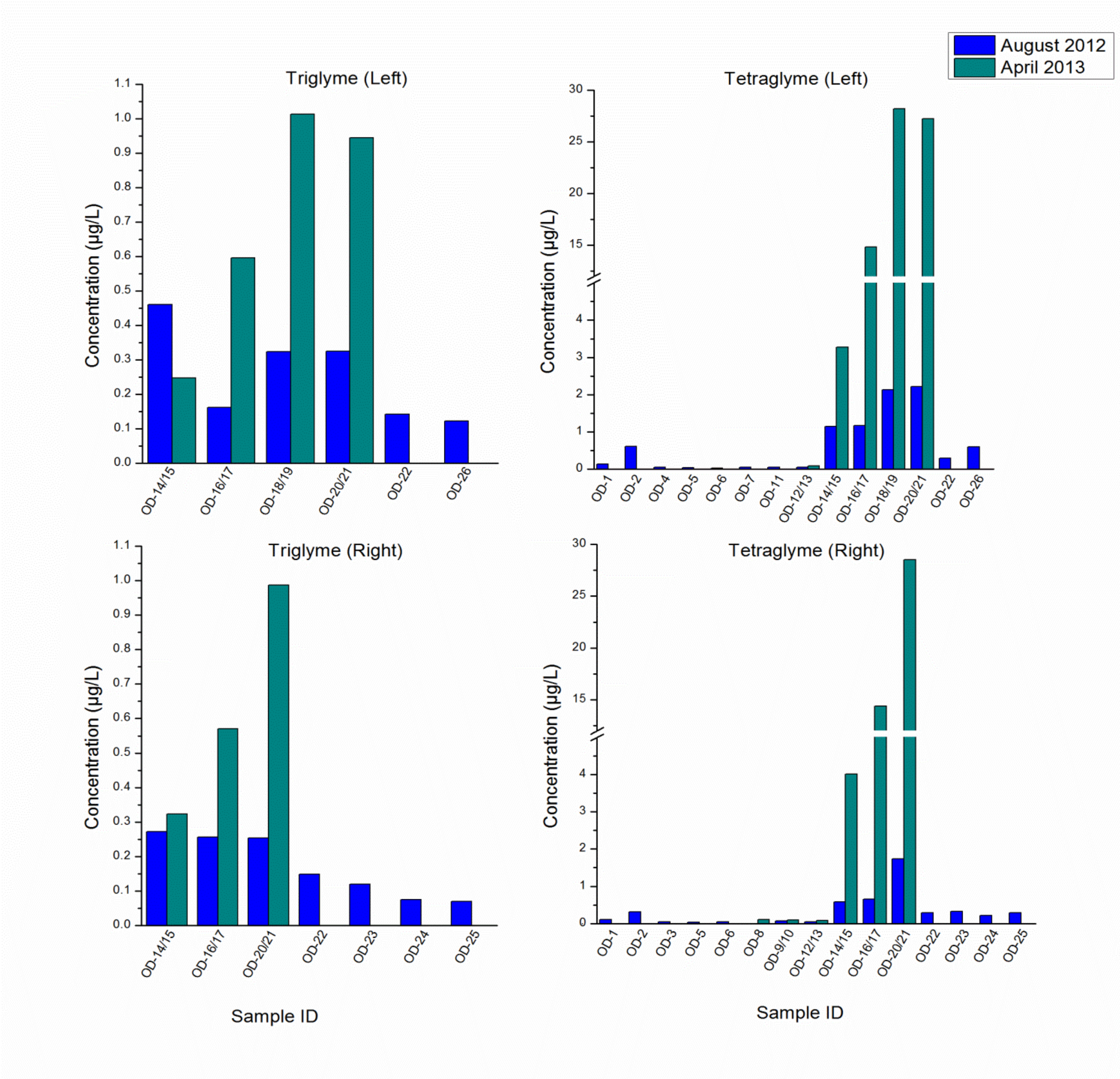


FIGURE 5.2 Concentration of triglyme and tetraglyme, in μg L^{-1}, on the left and right side of the Oder River during the sampling campaigns conducted in August 2012 and April 2013.

In order to calculate the load of diglyme, triglyme, and tetraglyme in the Oder River, discharge information was obtained from the Institute of Meteorology and Water Management in Poland and the Ministry of Environment, Health and Consumer Protection of the Federal state of Brandenburg, Germany (IMGW-PIB, 2013; LUGV, 2013). Information on discharge ($m^3\ s^{-1}$) of the Oder River was only available for few sampling locations (**Table 5.2**). **Fig. 5.3** demonstrates the loads ($kg\ d^{-1}$) of diglyme, triglyme and tetraglyme in the Oder River for all of the locations for which river discharge was available. The average load of diglyme in the Oder River equaled to 2.5 $kg\ d^{-1}$ (n = 7) and was, as expected, the lowest out of all investigated glymes. The load of triglyme was between 0.62 $kg\ d^{-1}$ and 37 $kg\ d^{-1}$. Tetraglyme was present in the Oder River between 1.79 $kg\ d^{-1}$and 680 $kg\ d^{-1}$. The highest load of diglyme (5.2 $kg\ d^{-1}$) and triglyme (37 $kg\ d^{-1}$) was calculated for the sampling performed in January 2012. During that time the discharge of the Oder River was over twofold greater than during the other sampling campaigns, reaching over 800 $m^3\ s^{-1}$ (**Table 5.2**). Also, in the samples collected in April 2013 the load of triglyme and tetraglyme in the Oder River was particularly high, with 24 $kg\ d^{-1}$ and 680 $kg\ d^{-1}$, respectively. At this time the discharge was close to 300 $m^3\ s^{-1}$. Additionally, it was observed that at locations sampled twice, OD-14/15 (km 331), OD-20/21 (km 429) and OD-29/30 (km 645) the load of the glymes increased with the increasing discharge of the river (**Fig. 5.3**). However, due to the lack of continuous data over a prolonged period, seasonal trends cannot be evaluated. Nevertheless, these results show that the load of glymes in the Oder River is not constant. The amount of glymes in the river might be dependent on the source of pollution, hence discharge of wastewater effluent into the river. The possible explanation for this observation is provided in Section 4.4.

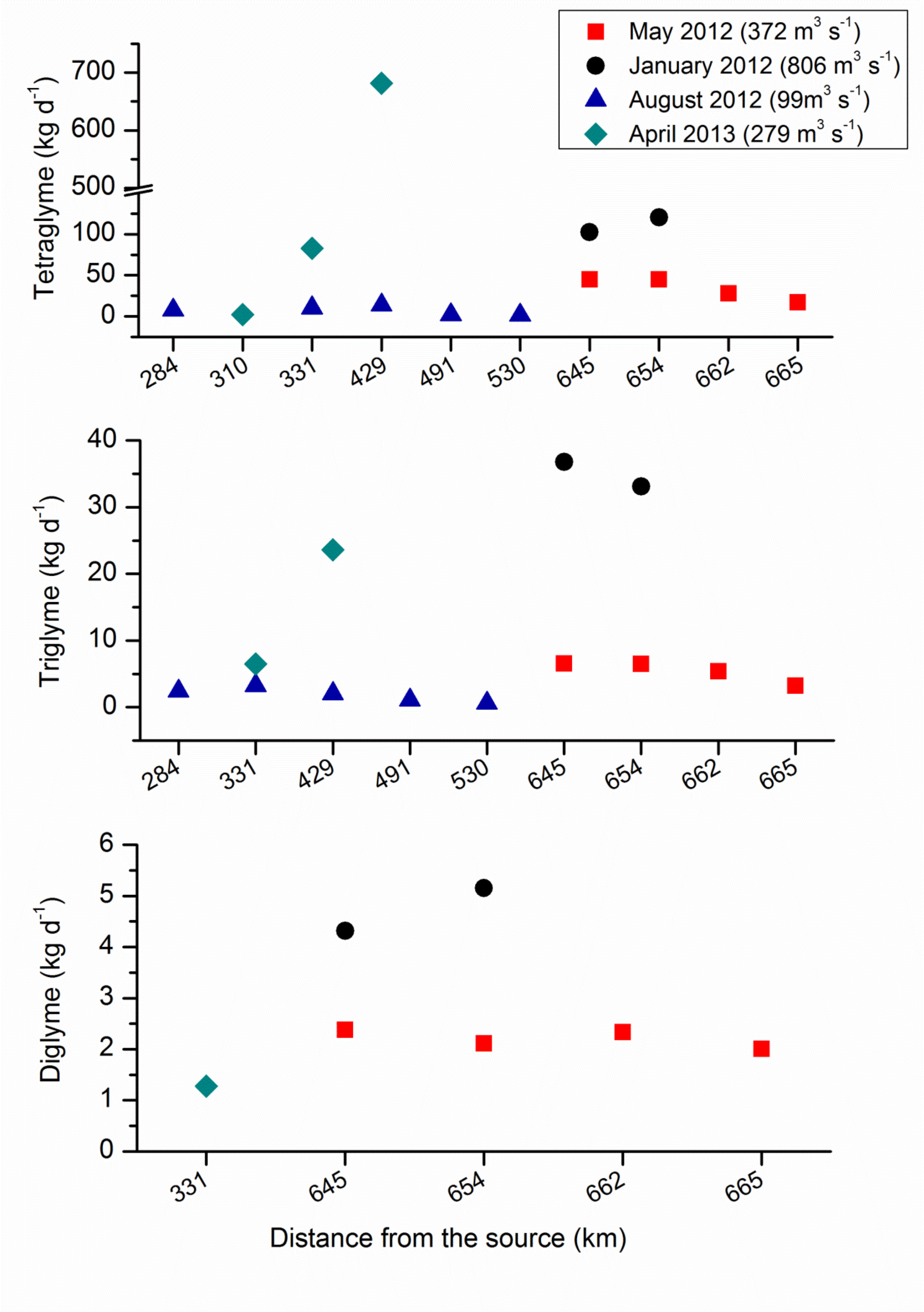


FIGURE 5.3 Load of diglyme, triglyme, and tetraglyme (in kg d^{-1}) in the Oder River.

5.5.2. Occurrence of glymes in tributaries

Based on the collected data, the entry point of the glymes into the Oder River was identified to arise between sampling locations OD−12/13 (km 310) and OD−14/15 (km 331). At these locations glymes were either first detected or their concentration radically increased in the river. Detailed research of the suspected area identified a large production facility for copper and silver that might be responsible for the pollution. Moreover, Kaczawa River is the only tributary of the Oder River in the suspected area. In April 2013, samples from Kaczawa River, and its tributary Czarna Woda stream were obtained to investigate if these surface water bodies contribute to the high glyme concentrations in the Oder River. **Fig. 5.4** illustrates the detected concentrations of the glymes in the Czarna Woda stream (CW1 & CW2), Kaczawa River (KW-1 & KW-2), and at the closest sampling locations of the Oder River (OD-13 & OD15). Samples from the Czarna Woda stream showed that concentrations at sampling point CW-2 were considerably higher than at CW-1, indicating that the glyme entrance in this region is located around sampling point CW-2. The detection of lower concentrations of both triglyme and tetraglyme at the CW-1 sampling point compared to CW2 might have occurred due to water mixing. Further investigations helped to identify the source of glymes in this area. The WWTP located in the proximity to the sampling area discharges its effluent into the creek entering the Czarna Woda stream close to the CW-2 sampling point. The Czarna Woda stream enters Kaczawa River in the city of Legnica. The concentration at KW-1 decreased twofold compared to CW-2, whereas the concentrations at KW-2 were similar to those at KW-1. As expected, the concentrations in the Oder River were much lower than in the tributaries, due to a dilution of surface waters. At the time of the sampling, the discharge of the Kaczawa River at KW-1 was 18 $m^3 s^{-1}$, whereas the discharge of the Oder River at OD−15 was 263 $m^3 s^{-1}$ (LUGV, 2013). The load in the tributary was calculated to equal to 4.1 kg d^{-1} (diglyme), 9.2 kg d^{-1} (triglyme), and 61 kg d^{-1} (tetraglyme). In the Oder River (OD−15), the average load based on the concentrations on the left and right side of the river was 1.3 kg d^{-1} for diglyme, 6.5 kg d^{-1} for triglyme, and 83 kg d^{-1} for tetraglyme. Information on average yearly discharge is not readily available for Czarna Woda. The variations in the loads between the tributary and the Oder River might be explained by a dilution as well as variations in the sampling period. The samples from the Oder River at OD−15 were obtained the day before the tributary sampling. The Kaczawa River is an important source of drinking water for the city of Legnica. Through bank filtration and additional water treatment processes, about 18,000 m^3 of drinking water is produced daily. The surface water is withdrawn several km before the Czarna Woda stream discharges into Kaczawa River.

Nevertheless, one drinking water sample collected during the sampling campaign in April 2013 showed a concentration of 0.092 µg L^{-1} for triglyme and 0.36 µg L^{-1} for tetraglyme. Based on the oral DNEL for triglyme (3.13 mg/kg bw/day), this concentration does not pose a risk to the general population living in the area. Assuming that an individual person weighs 70 kg and consumes 2 L of water per day, over a 75 year lifespan, the concentration that could cause reproductive and developments effects equals to 93,000 µg L^{-1} for triglyme (ECHA, 2012). Nevertheless, the Kaczawa River should be protected from large effluent discharges, due to its proximity to the drinking water production facility. Although the river water is subject to bank filtration before additional drinking water treatments, based on the previous investigations by Stepien et al. (2013) glymes are not readily attenuated during bank filtration. Additional water sampling is necessary to determine the extent of drinking water contamination with glyme compounds in the area.

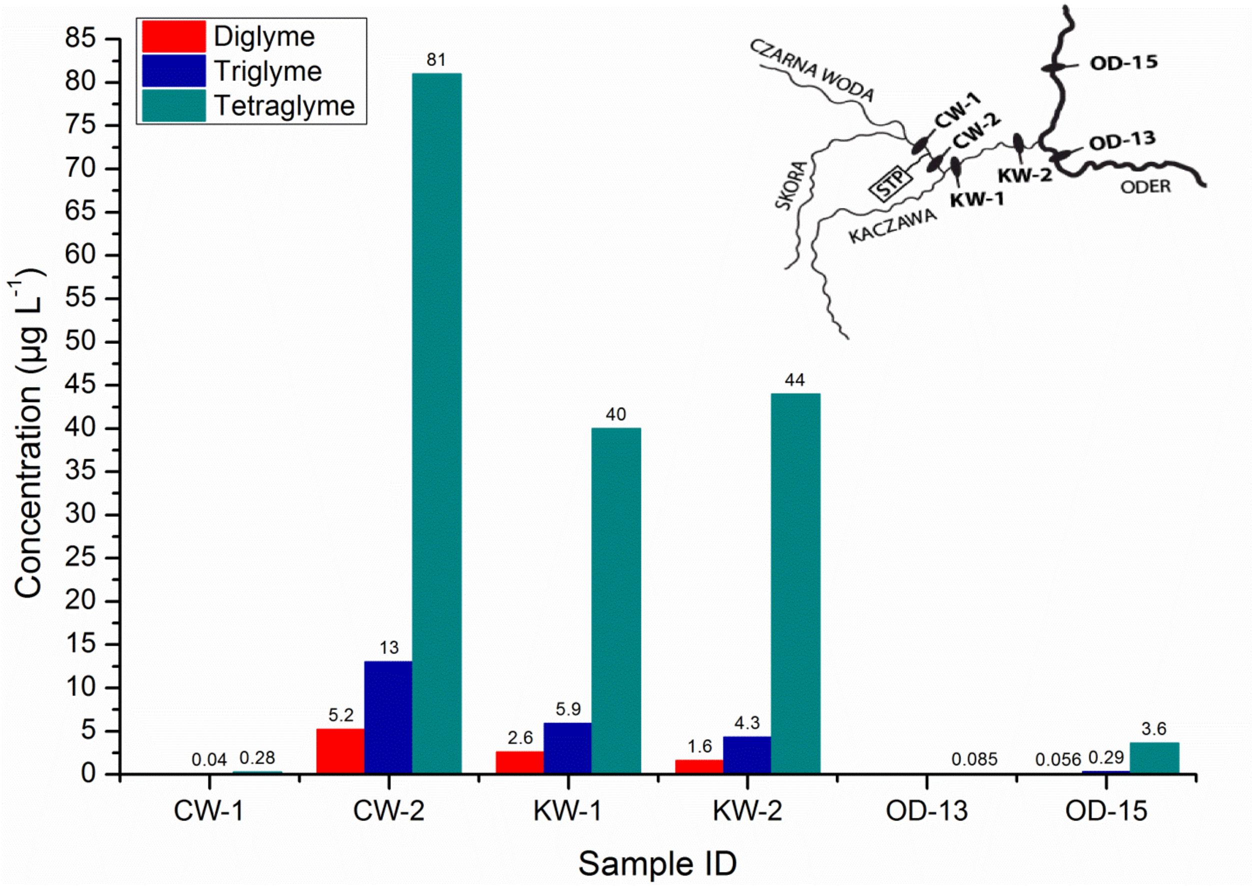


FIGURE 5.4 Concentrations of glymes (µg L^{-1}) in the Oder River (OD), Czarna Woda stream (CW) and Kaczawa River (KW) during April 2013 sampling campaign.

5.5.3. Glymes in the investigated industrial wastewater

Three manually collected grab wastewater samples were obtained from a WWTP that receives effluents from nearby industries, among which is the Legnica Copper Smelter and Refinery. In order to combat the extremely high atmospheric pollution with sulfur dioxide, Legnica Copper Smelter and Refinery installed a gas desuphurization Solinox plant in 1994. The German company Linde AG developed the Solinox process, in which a mixture of homologes of polyglycol dimethyl ethers (glymes), marketed under the name Genosorb®1900 is used as a physical scrubbing solvent for the purification of vent gases from sulfur dioxide (Heisel and Belloni, 1991; Sporer, 1992). At the Legnica Copper Smelter and Refinery gases from the shaft furnaces generated from the copper production are first dedusted and then used at the local heat and power plant. Next the gases are desulfurized in the Solinox installation and the recovered SO2 is used in the sulfuric acid plant (Szczęśniak, 2000). Additionally, the off-gases from the sulfuric acid plant are also treated in the Solinox process.

The wastewater produced by this process is treated in the investigated WWTP. Following the mechanical and chemical treatment, the effluent of the WWTP is discharged into a small creek that enters Czarna Woda stream. Table 4shows glyme concentrations in the three wastewater samples (WW-1, WW-2, WW-3) from unidentified unit operations in the WWTP investigated. The concentrations of diglyme ranged from 1 μg L^{-1} to 1700 μg L^{-1}, triglyme 63 μg L^{-1} to 13,000 μg L^{-1}, and tetraglyme from 810 μg L^{-1} to 190,000 μg L^{-1}. The effluent sample was not made available by the WWTP. The limited, but sufficient data verified that the investigated WWTP is the major cause of glyme pollution in the investigated surface waters. The PNEC value established (6400 μg L^{-1}) was exceeded for triglyme and tetraglyme in these samples. However, considering the dilution of the concentrations resulting after the discharge of the wastewater into the surface waters, glyme concentrations can be expected to have no predicted effect on the environment. The investigated industrial WWTP employs only chemical and mechanical treatment, hence removal of glymes is not expected and a mixture of the sampled wastewaters is most likely reaching the receiving surface water. Nevertheless, according to the published studies, biological treatment also does not ensure complete removal of polyethylene glycol ethers from wastewaters (Roy et al., 1994; Fischer and Hahn, 2005; Beschkov et al., 1997; Kawai, 2002).

Table 5.4 Concentration (μg L^{-1}) and load (kg d^{-1}) of diglyme, triglyme and tetraglyme in the three wastewater (WW) samples from the WW treatment plant treating effluents from a Solinox process.

	WW-1	WW-2	WW-3
Analyte	Concentration (μg L^{-1})		
Diglyme	14	1.0	1700
Triglyme	230	63	13,000
Tetraglyme	6300	810	190,000
	Load (kg d^{-1})		
Diglyme	0.050	0.004	6.4
Triglyme	0.87	0.24	48
Tetraglyme	24	3.1	730

5.5.4. Gas desulphurization as a source of glyme pollution

About 450 m^3/h of a solvent circulates within the Solinox installation in the Legnica Copper Smelter and Refinery (Czubak, 2005). According to Harasimowicz et al. (2005) and Czubak (2005), the composition of a Genosorb® 1900 changes during regeneration of the solvent. A fresh solvent makes up less than 5% of triglyme, 72−75% of tetraglyme, 16% of pentaglyme and the rest consist of higher glymes (Czubak, 2003). The regenerated solvent composition changes to: 1% of triglyme, 35−40% of tetraglyme, 40−45% of pentaglyme and about 15% of higher glymes. Hence, the proportion of triglyme to tetraglyme in the fresh solvent is about 6.6%, whereas in the used solvent it is about 2.5%. In the wastewater samples collected, the proportion of the two glymes is between 3.6% and 7.8%, being close to the expected value. Diglyme was not reported as a component of the Genosorb® 1900 solvent, therefore it is expected to be present as a degradation product formed during solvent regeneration or solvent storage. Oxygen is responsible for the degradation of the sorbent, resulting in shorter glyme chains (ex. diglyme) as well as ester groups, aldehydes, hydroxyl groups, alcohols, water and carboxylic acids (Wenger et al., 1999; Geiger and Becker, 1999).

According to Harasimowicz et al. (2005), 20,000 m3 of wastewater is produced annually by the Solinox process, containing about 40 tons of Genosorb®1900. Czubak (2005) reported that 77 tons of solvent is lost each year at the Legnica Copper Smelter and Refinery. Based on the three samples made available by the wastewater treatment plant, the average total load of diglyme, triglyme, and tetraglyme in the wastewater was calculated to equal 98 tons per year (higher glymes not included in the calculation), considering that 1,400,000 m3 of wastewater is treated in the WWTP annually. This average load calculated for the three glymes exceeds the 40 tons stated by Harasimowicz et al. (2005) and 77 tons reported by Czubak (2005). The load of the Genosorb®1900 solvent in the wastewater is contingent on the maintenance of the Solinox installation and the waste produced by the process itself (Czubak, 2005). Hence, the variability of the glyme concentration in the wastewater and the fluctuating discharge of the Oder River may explain the high load variation of glymes in the Oder River. The average total load of diglyme, triglyme and tetraglyme in the Oder River was determined to be about 40 tons per year, being in good agreement with an average load of Genosorb®1900 in the wastewater reported by Harasimowicz et al. (2005), noting that higher glymes were not analyzed. At the time of the sampling, the total load of the three glymes in the Kaczawa River was 75 kg d^{-1}, hence 27 tons per year. The limited number of samples collected from the rivers and the WWTP constrain detailed comparison of the results.

The problem of the solvent loss in the Solinox process, hence contamination of surface waters, has already been addressed. Harasimowicz et al. (2005) used a process of selective reverse osmosis and was able to recover 96% of the ether solvent from wastewater produced during a Solinox process. Liang et al. (2004) showed an effective pervaporation of monoglyme from aqueous solutions on cross lined oligosilylstyrene-PDMS composite membranes. If such processes were implemented in the Solinox installation in Legnica, the loss of solvent could be reduced and the discharge of effluents containing high glyme concentrations into surface waters may appreciably decrease.

5.6. Conclusions

The results of the current study provide information on the occurrence of diglyme, triglyme and tetraglyme in the Oder River. By tracking the high concentrations in the Oder River, the main source of contamination was localized in the area of Legnica city. Wastewater treatment plant, treating effluents originating from the Solinox process was found responsible for the high glyme concentrations in the Oder River and its tributaries. The Solinox process is a physical absorption process, which removes SO2 from flue gases using a mixture of glymes as a physical solvent. The amount of glymes in the wastewater is contingent on the maintenance of the Solinox installation and the waste produced by the process itself. Hence, the load of glymes in the surface waters is expected to correlate with the amount of glymes in the influents received and effluents discharged by the WWTP as well as the discharge (water flow) of the river. The issue of high solvent loss during the Solinox has already been addressed and an improved technique for their recovery from the wastewater will hopefully be implemented in the near future in order to protect receiving surface waters.

Chapter 6 Summary, conclusions and outlook

6.1. Summary

The focus of the presented doctoral thesis was to 1. Develop a suitable method for determination of six hydrophilic ethers: ETBE, 1,4-dioxane, monoglyme, diglyme, triglyme, and tetraglyme; 2. Determine the behavior of hydrophilic ethers during bank filtration and in the anoxic aquifer system; 3. Investigate the distribution of 1,4-dioxane in the aquatic environments and to 4. Study the occurrence and identify sources of glymes in the Oder River. These topics were discussed in the following chapters:

Chapter 2 **Method development for hydrophilic ethers:** The proposed analytical method based on SPE and GC/MS-SIM provided excellent recoveries, reproducibility and low detection limits (in ng L^{-1} range) for ETBE, 1,4-dioxane, monoglyme, diglyme, triglyme, and tetraglyme. This was the first time that a SPE method was applied for the analysis of ETBE, which is considered as volatile substance, for which in general headspace analysis is applied. Nevertheless, the recoveries of the SPE method for ETBE were as high as those known from headspace analytical methods. Moreover, this method can be extended for analysis of other ether compounds that might be of significance to the environment and/or human health. The extensive use of ETBE, 1,4-dioxane, and glymes in Europe and their persistent physicochemical properties call for their continuous monitoring in the aquatic environment. During this research project, 27 samples from seven surface water bodies were obtained for quantitation of the six target substances. Especially, outstanding were the high concentrations (reaching 2.00 µg L^{-1}) of 1,4-dioxane in all of the waters investigated. The high concentrations of selected glymes in the Oder River also requested further investigation.

Chapter 3 **Behavior of 1,4-dioxane and glymes during bank filtration and in the anoxic aquifer:** In this study the behavior of ethers during infiltration of the Oder River into the Oderbruch aquifer was compared to the behavior of chlorinated and non-chlorinated organophosphates. The results of four sampling campaigns performed between 2009 and 2012, showed a much greater persistence of ethers both in the main drainage ditch (after bank filtration) and in the anoxic aquifer. Moreover, ethers such as triglyme, tetraglyme, and 1,4-dioxane were detected further from the Oder River and in older ground waters than any of the OPs. Tetraglyme was present in the shallow groundwater of the Oderbruch with an estimated age of 21 years within 27 and 60 ng L^{-1} and 1,4-dioxane in a 34.9 year groundwater (deep well) at a concentration above 200 ng L^{-1}. Moreover, these two ethers showed a high correlation with the frequently used inorganic tracer chloride, hence their possible application as organic tracers to study the dynamics of the groundwater system. Additionally, possible biodegradation and attenuation processes of OPs and ethers were discussed based on the obtained data.

***Chapter 4* Distribution of 1,4-dioxane in the aquatic environments:** As presented in Chapter 1 and 2, 1,4-dioxane showed a ubiquitous presence in the surface waters. Initially, the contribution of sewage treatment plants (STPs) to the high concentrations of 1,4-dioxane in the rivers was investigated. The maximum influent concentrations in the four investigated STPs reached only 834 ± 480 ng L^{-1}. Surprisingly, the effluent concentration of 1,4-dioxane was determined to be 62,260 ± 36,000 ng L^{-1}. An extensive sampling of the STP responsible for the high effluent concentrations, showed that the methanol used in the postanoxic denitrification process contains high amount of impurities, among which was 1,4-dioxane. Moreover, spatial and temporal distribution of 1,4-dioxane in the Main, Rhine, and Oder River, showed that the concentration of 1,4-dioxane increases with a distance from the spring of the river. A two week investigation of the Rhine River at the monitoring station in Worms demonstrated that the 1,4-dioxane concentration decreases with an increasing discharge of the river. Based on the results from the groundwater study in the Oderbruch polder presented in Chapter 3, that showed the natural bank filtration is not capable of removing 1,4-dioxane from water, two drinking water facilities that utilize bank filtration in drinking water production were investigated. 1,4-Dioxane was present in the raw water samples collected after bank filtration at concentration close to or at 650 ng L^{-1} and after drinking water treatment processes at 490 ng L^{-1} and 600 ng L^{-1}.

***Chapter 5* Occurrence and sources of glymes in the Oder River.** Based on the high concentrations of especially triglyme and tetraglyme in the Oder River reported in Chapter 2, an investigation of possible glyme sources was initiated. The extensive sampling campaigns of the Oder River in Poland and Germany helped to identify the region of glyme entry and the predominating source of contamination. In the Oderbruch polder area, concentrations of diglyme, triglyme, and tetraglyme were determined at 0.07 µg L^{-1}, 0.54 µg L^{-1} and 1.73 µg L^{-1}, respectively. During the subsequent sampling in Poland, when samples from almost 500 km of the river were collected, triglyme was present at a maximum concentration of 0.46 µg L^{-1} and tetraglyme at 2.21 µg L^{-1}. At the same time, the area of the glyme entry into the Oder River was identified, and the final sampling campaign focused also on the tributaries: Czarna Woda stream and the Kaczawa River. The concentrations in Czarna Woda reached 5.18 µg L^{-1}, 12.87 µg L^{-1} and 80.81 µg L^{-1} for diglyme, triglyme, and tetraglyme, respectively. Finally, three wastewater samples from an industrial wastewater treatment plant were collected. The average concentration of diglyme was 569 µg L^{-1}, triglyme 4300 µg L^{-1}, and tetraglyme 65900 µg L^{-1}. Further research identified a gas desulfurization process (Solinox) used in the nearby copper smelter, to be responsible for the high concentrations of glymes in the tributaries and in the Oder River. Glymes are used as physical absorption media for the removal of sulphur dioxide from the flue gases.

6.2. Conclusions

This doctoral thesis focused on providing information about the occurrence, distribution and behavior of ETBE, 1,4-dioxane and glymes in the major rivers in Germany and Poland. The conclusions of the research projects follow:

ETBE

In the investigated rivers in Germany and in the Oder River (Poland) ETBE was present at concentrations close to or below detection limit. As mentioned in Chapter 1, in Germany MTBE has been replaced by ETBE in 2005, but currently ethanol is blended directly with the gasoline. Nevertheless, ETBE is known to be extensively used in other European countries such as Spain, France, and Italy, where its entrance into an aquatic environment might be of concern. Many environmental aspects of ETBE are comparable with MTBE, except that ETBE is likely to show even lower evaporation from water due to its higher boiling temperature and lower vapor pressure. An extensive research has been done on the occurrence, behavior and fate of MTBE in the aquatic environment, since high concentrations in surface-, ground- as well as drinking water were reported. In order to ensure that ETBE does not pose a risk to public water supplies its occurrence should also be regularly monitored particularly in countries that still use ETBE as an anti-knocking additive for gasoline.

1,4-DIOXANE

Based on the data obtained in this study from the waste-, surface-, ground-, and drinking waters it can be concluded that 1,4-dioxane is an extremely persistent organic pollutant. Its widespread presence in the aquatic environment and the high concentrations detected necessitate continuous monitoring. The results from the four investigated sewage treatment plants show that the amount of 1,4-dioxane in the influents does not exceed 1000 ng L^{-1}. Possibly, this quantity originate from the personal care products used in many households that reportedly contain 1,4-dioxane as a production byproduct (Chapter 1 & 4). In one out of the four investigated STPs, addition of methanol during the postanoxic denitrification process resulted in extremely high concentrations of 1,4-dioxane in effluents (62,260 ± 36,000 ng L^{-1}). The source and purity of the methanol needs to be a part of a quality control in the STPs in order to prevent discharge of high concentrations of 1,4-dioxane into the receiving surface waters. Since the STP investigated used a recycled methanol from unknown industries it is most likely that 1,4-dioxane in not efficiently removed from the methanol. 1,4-dioxane forms an azeotropic mixture with methanol, hence simple distillation will not separate them from each other and alternative solvent recovery methods might not be able of separating them completely. The load of 1,4-dioxane from this STP was calculated to be between 2.17 to 5.03 kg d^{-1}. The average load in the Main, Oder and Rhine River was determined in this study to be 6.5 kg d^{-1}, 34.1 kg d^{-1} and 134.5 kg d^{-1}, respectively. This high load of 1,4-dioxane in the Main River cannot be solely explained with the results from the investigated STP, hence it can be expected that other major sources of 1,4-dioxane exist. Further industrial effluents might contain high concentration of 1,4-dioxane as a by-product such as PET plastic production, ethoxylation and synthesis of polyesters. Manufacturer supposedly use vacuum stripping process in order to remove 1,4-dioxane from their effluents, however studies are not available in order to assess if this removal process effectively reduces the amount of 1,4-dioxane from effluents.

The importance of regulating high concentrations of 1,4-dioxane in the effluents discharged into the surface waters is reflected in its effortless transfer to drinking water sources. As discussed in Chapter 4, bank filtration is often utilized as a first major treatment process of surface water for the subsequent production of drinking water. This technique is often used in Germany as well as other countries around the world. Consequently, protection of surface waters from pollution with toxic or carcinogenic substances is crucial. The average concentration of 1,4-

dioxane in the Rhine River in this study was calculated to be 470 ng L^{-1} however it varies with the discharge of the river. The concentration of 1,4-dioxane in the Rhine River often surpasses 1000 ng L^{-1} (**Figure 4.9**), which is a proposed target value by IAWR for contaminants in surface water used in the production of drinking water. The concentration of 1,4-dioxane in the drinking water depends on the concentrations occurring in the river and on the local drinking water treatment methods. In the two raw water samples collected in this study from drinking water treatment facilities, the concentration of 1,4-dioxane was 650 ng L^{-1} and 670 ng L^{-1}. Following various treatment technologies applied at the two drinking water treatment facilities the concentrations fell only slightly to 600 ng L^{-1} and 490 ng L^{-1}, respectively. The concentration of 1,4-dioxane exceeded the precautionary guidance limit of 100 ng L^{-1} in drinking water proposed by the German Federal Environmental Agency. Moreover, U.S. EPA proposed a minimum reporting level (MRL) for 1,4-dioxane in drinking water at 70 ng L^{-1}, as a part of Unregulated Contaminant Monitoring Rule 3. The analysis of 1,4-dioxane in drinking water is expected to become of great importance in the future.

Furthermore, the results show that conventional treatment technologies are not capable of removing 1,4-dioxane below the precautionary guidance limit of 100 ng L^{-1} in drinking water proposed by the German Federal Environmental Agency. Numerous studies have documented advanced oxidation processes to be a promising remedial technology for 1,4-dioxane. Especially H_2O_2/UV proved to be a viable treatment process for 1,4-dioxane and many other persistent water contaminants. Hence, drinking water production from sources known to contain an elevated amount of compounds resistant to degradation such as 1,4-dioxane should employ AOP in their treatment technologies.

As of the beginning of this research project, the occurrence of 1,4-dioxane in the aqueous environment in Germany was not known. The detection of high concentrations of 1,4-dioxane in surface waters was surprising and lead to numerous important findings. This doctoral thesis provided a foundation for further studies required with respect to the sources and behaviour of 1,4-dioxane in the aquatic environment.

GLYMES

This was the first study that focused primarily on the occurrence of glycol diethers in the aquatic environment. Based on the results from the first surface water sampling campaign (Chapter 2) in Germany, the occurrence and concentrations of monoglyme, diglyme, triglyme, and tetraglyme vary significantly in rivers. Concentrations of glymes in the Rhine River (Chapter 2) during this study were below 0.500 µg L^{-1} for monoglyme, and 0.200 µg L^{-1} for diglyme, triglyme, and tetraglyme. In the past, concentrations reaching 10.0 µg L^{-1} for diglyme, 5.0 µg L^{-1} for triglyme, and 2.5 µg L^{-1} tetraglyme were detected in the Rhine River (**Figure A.2)**. Although the industry responsible for the discharge of glymes into the Rhine River was identified, no other information was made public. Tetraglyme was also detected in the Main and Rur River at an average of 0.409 µg L^{-1} ($n = 6$) and 0.192 µg L^{-1} ($n = 1$), however the possible sources there were not identified. The wide range of industrial applications of glymes makes it difficult to establish their origin in the surface waters. The high concentrations of diglyme (0.07 µg L^{-1}), triglyme (0.54 µg L^{-1}), and tetraglyme (2.21 µg L^{-1}) in the Oder River encouraged investigation of their source. The extensive sampling campaigns of the Oder River as well as its tributaries and samples from the wastewater treatment were required in order to establish the cause of high glyme concentrations and to identify the area and source of pollution. At the Copper Smelter and Refinery in Legnica, PL, Solinox installation was installed in 1994 and as a result the pollution of the Oder River with the glycol diethers begun (Chapter 5). This information is supported by the data obtained during the study of the bank filtration and ground water passage at the Oderbruch polder (Chapter 3). Tetraglyme was detected in the groundwater with an estimated age of 21 years, but not in any of the older wells. As reported by Clariant (2013), flue gas desulfurization techniques utilizing glymes as physical absorption media are commonly used in Europe. Therefore it can be expected, that unless proper solvent recovery techniques are implemented within the process, other surface waters might be affected by glyme pollution.

Moreover, the persistence of glymes in the aquatic environment was demonstrated in Chapter 3. Both triglyme and tetraglyme were present at significant concentrations in the groundwater of the Oderbruch polder following bank filtration. Furthermore, the similarities in the behavior of Cl^{-} and tetraglyme show that they are controlled by the same or similar hydraulic process. The correlation factor of Cl^{-} with tetraglyme was calculated to be $r = 0.613$, which is lower than for 1,4-dioxane ($r = 0.913$), however according to the results presented in Chapter 5, the concentrations of tetraglyme in the Oder River are influenced by the highly variable effluent concentrations of the wastewater treatment plant responsible for glyme pollution. As previously mentioned glymes are toxic to reproduction and as shown are not easily removed from water during natural attenuation processes. Moreover, they are not likely to undergo biodegradation. Therefore, it can be concluded that AOPs would need to be applied in order to remove them from effluents. Water bodies that are used for drinking water production should be protected from high concentrations of these ethers. In the Rhine River the problem of glyme pollution was relatively quickly addressed and solved. The solution for the pollution of the Rhine River with 1,4-dioxane seem to be more complex.

The most important contribution of the present study on glymes was the establishment of their sources in the Oder River. No other publication was found that identified origin and pollution of surface waters with glymes. Nevertheless, other major sources of glymes in the environment exist and still need to be determined.

6.3. Outlook

Many topics have been addressed in the presented doctoral thesis. Some research questions stated in Chapter 1 (Section 1.4) have been answered completely and some still require further investigations in order to better understand the behavior of the hydrophilic ethers (Chapter 3) and to determine other possible sources of these compounds in surface waters (Chapter 4 & 5). Nevertheless, the work presented contributed greatly to the knowledge on the occurrence, distribution, and behavior of hydrophilic ethers (1,4-dioxane and glymes) in the aquatic environment.

According to the results presented in Chapter 3 and 4, 1,4-dioxane and glymes are not readily attenuated during bank filtration and persist in the anoxic aquifer. The data collected at the Oderbruch polder from the shallow and deep groundwater wells situated at increasing distance from the river, showed that ethers such as 1,4-dioxane and tetraglyme remain in the groundwater much longer than other organic compounds such as organophosphates. The sampling scheme did not take into account the travel time of water from the river into the main drainage ditch; therefore the degree of attenuation of ethers during bank filtration could not be established. Long term monitoring study in the Oderbruch polder is required to determine if any of the attenuation processes in the reducing aquifer are able to decrease the concentrations of ethers. The influence of redox conditions in the aquifer on the degradability of ethers was not established based on the collected data. Only the presence of degradation products would enable to verify the extent of ether biodegradation, if any, in the anoxic aquifer.

In order to explain the high load of 1,4-dioxane in the surface waters, the effluent concentration of other municipal as well as industrial wastewater treatment plants need to be investigated. In a view of the fact that 1,4-dioxane may reach potable water it would be advisable to perform a nationwide study, to determine if many drinking water sources, produced from the managed aquifer recharge, are affected by significant concentrations of 1,4-dioxane. Moreover, it would be of interest to investigate a drinking water treatment plant that applies advanced oxidation processes in order to observe the extent of 1,4-dioxane removal from drinking water.

Glymes are reportadly used as physical absorption media in many parts of Europe. Genosorb® 1753 is used for H_2S removal in plants situated in proximity to Weser and Ems Rivers in Germany. It would be of interest to determine if pollution with glymes also occurs in these rivers. Moreover, both monoglyme and tetraglyme were identified in the Main River. Especially, high concentrations reaching 1.25 µg L^{-1}, were detected for tetraglyme, therefore a significant source of this glyme must exist upstream from the city of Frankfurt/Main and should be determined.

References

Abe A.Distribution of 1,4-dioxane in relation to possible sources in the water environment. Sci Total Environ **1999**, 227, 41-47.

Achten C., Kolb A., Püttmann W. Occurrence of methyl *tert*-butyl ether (MTBE) in riverbank filtered water and drinking water produced by riverbank filtration. Environ Sci Technol **2002**, 36, 3662-3670.

Adams C.D., Scanlan P.A., Secrist N.D. Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone. Environ Sci Technol **1994**, 28, 1812-1818.

Agency for Toxic Substances and Disease Registry. Toxicological profile for 1,4-dioxane. **2012**. Atlanta, Georgia.

Amy G. & Drewes J. Soil aquifer treatment (SAT) as a natural and sustainable wastewater reclamation/reuse technology: fate of wastewater effluent organic matter (EfOM) and trace organic compounds. Environ Monit Assess **2007**, 129, 19-26.

Barker J.F., Hubbard C.E., Lemon L.A. The influence of methanol and MTBE on the fate and persistence of monoaromatic hydrocarbons in groundwater. Proceedings of the 1990 API/NWWAConference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, **1990**, 113-127.

Basberg L., Banks D., Saether O.M. Redox processes in groundwater impacted by landfill leachate. Aquat Geochem **1998**, 4, 253-272.

Beckett M.A. and Hua I. Enhanced sonochemical decomposition of 1,4-dioxane by ferrous iron. Water Res **2003**, 37, 2372-2376.

Benson J, Cicolella A, Dujardin R. Improved extraction of glycol ethers from water by solid-phase micro extraction by carboxen polydimethylsiloxane-coated fiber. Chromatographia **1999**, 50, 155-159.

Beschkov V.,Bardarska G., Gulyas H., Sekoulov I. Degradation of triethylene glycol dimethyl ether by ozonation combined with UV irradiation or hydrogen peroxide addition. Water Sci Tech **1997**, 36, 131-138.

Bester K. and Schäfer D. Activated soil filters (bio filters) for the elimination of xenobiotics (micro-pollutants) from storm- and waste waters. Water Res **2009**, 43, 2639-2646.

Black R.E., Hurley F.J., Havery D.C. Occurrence of 1,4-dioxane in cosmetic raw materials and finished cosmetic products. J AOAC Int **2001**, 84, 666-670.

Borch T., Kretzschmar R., Kappler A., Cappellen, P.V., Ginder-Vogel, M., Voegelin, A., Campbell, K. Biogeochemical redox processes and their impact on contaminant dynamics. Environ Sci Technol **2009**, 44, 15-23.

Bradley P.M., Chapelle F.H., Landmeyer J.E. Methyl- t-butyl ether mineralization in surface-water sediment microcosms under denitrifying conditions. Appl Environ Microbiol **2001a**, 67, 1975-1978.

Bradley P.M., Chapelle F.H., Landmeyer J.E. Effect of redox conditions on MTBE biodegradation in surface water sediments. Environ Sci Technol **2001b**, 35, 4643-4647.

Budavari S., O'Neil M.J., Smith A., Heckelman, P.E. The Merck Index, 11th ed. **1989**, Merck & Co. Inc., Rahway, NJ, 954.

Burmaster, D.E. The new pollution-groundwater contamination. Environment **1982**, 24, 33-36.

Cao X.L.and Zhu, J. Monitoring method for airborne glymes and its application in fuel exhaust emission measurement. Chemosphere **2001**, 45, 911-917.

Chemischen und Veterinäruntersuchungsämter Karlsruhe und Freiburg. Verunreinigung kosmetischer Mittle mit 1,4-Dioxan (1,4-diethylendioxid): Welche Gehalte sind technisch vermeidbar. **2011**. Retrieved July 20, 2011, from http://www.ua-bw.de/pub/beitrag.asp?subid=2&Thema_ID=4&ID=1451&Pdf=No.

Chiang D. S.-Y., Everett W.G. Jr., Peterman J., Harrigan J., DiGuiseppi B., Woodward, D.S., Evaluation of natural attenuation at a 1,4-dioxane-contaminated site. Remediation **2008**, DOI; 10.1002.rem, 19-37.

Clariant. BU IC5, Engineering & Aviation. Powerpoint presentation by Clariant on Genosorb®. **2009**. Retrived on January 25, 2015, from http://www.dfhk.fi/fileadmin/ahk_finnland/Veranstaltungen/2010/AHK_Geschaeftsreise_Biogas/Clariant2.pdf.

Clariant. Products for gas treatment process. **2013**. Retrived January 25, 2013, from http://www.clariant.com/C12576720021BF8F/vwWebPagesByID/22AECBB9BC8750B4C12576FE002D520C.

Cox M.H., Su G.W., Constantz J. Heat, chloride, and specific conductance as ground water tracers near streams. Ground Water **2007**, 45, 187-195.

Czubak, A. Bezopadowa metoda odsiarczania gazow Solinox – wady I zalety. Rudy Metale **2003**, 48, 225-227.

Czubak, A., Analiza strat sorbentu dwutlenku siarki na instalacji Solinox. In: Grzesiak, P.; Schroeder, G.; Pruszyński, S., editors. Kwas Siarkowy – Nowa rzeczywistość. IOR Poznań, **2005**, ISBN: 83-89867-40-0.

Deeb R.A., Chu K-H., Shih T., Linder S., Suffet I., Kavanaugh, M.C., Alvarez-Cohen, L. MTBE and other oxygenates: environmental sources, analysis, occurrence, and treatment. Environ Eng Sci **2003**, 20, 433-447.

Department of Natural Resources Indiana. Ground-water resources in the White and West Fork White River Basin, Indiana. **2002**, Indianapolis, Indiana.

Díaz-Cruz M.S., Barceló D. Trace organic chemical contamination in ground water recharge. Chemosphere **2008**, 72, 333-342.

Dodson R.E., Perovich L.J., Covaci A., Van den Eede N., Ionas A.C., Dirtu A.C., Brody J.G., Rudel R.A.. After the PGDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ Sci Technol **2012**, 46, 13056-13066.

Doherty R.E. A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 2 - Trichloroethylene and 1,1,1-trichloroethane. Environ Forensics **2000**, 1, 83-93.

Duft M., Tillmann M., Oehlmann J. Ökotoxikologische Sedimentkartierung der großen Flüsse Deutschlands. Umweltbundesamt **2002**, Berlin, Germany.

European Centre for Ecotoxicology and Toxicology of Chemicals [ECETOC]. The Toxicology of glycol ethers and its relevance to man, Volume I and II. Technical Report No. 95, **2005**, Brussels, Belgium, ISSN-0773-8072-95.

European Chemicals Agency. Annex XV dossier - Identification of diglyme (DEGDME) as SVHC. Retrived December 12, **2011a**, from: http://echa.europa.eu/documents/10162/13640/svhc_axvrep_austria_belgium_poland_cmr_diglyme_20110829_en.pdf.

European Chemicals Agency. Annex XV – Identification of EGDME as SVHC. Retrieved December 12, **2011b**, from http://echa.europa.eu/documents/10162/13638/svhc_axvrep_egdme_203-794-9_en.pdf.

European Chemicals Agency. Annex XV – Identification of triglyme as SVHC. Retrieved December 12, **2011c**, from http://echa.europa.eu/documents/10162/13638/svhc_axvrep_tegdme_203-977-3_en.pdf.

European Chemicals Agency. Information on monoglyme, diglyme, triglyme, and tetraglyme. Retrieved September 1, **2013**, from http://echa.europa.eu/en/information-on-chemicals.

European Commission. European Union Risk Assessment Report: 1,4-dioxane. **2002**. The Netherlands. Retrieved March 20, 2013, from http://echa.europa.eu/documents/10162/a4e83a6a-c421-4243-a8df-3e84893082aa.

European Commission. EU Risk Assessment Report, Tris(2-chloroethyl) phosphate, TCEP (Draft). **2006**; Available through ORATS (Online EUropean Risk Assessment Tracking System).

European Commission. EU Risk Assessment Report, Tris(2-chloro-1-(chloromethyl)ethyl) phosphate, TDCP (Draft). **2007a**; Available through ORATS (Online EUropean Risk Assessment Tracking System).

European Commission. EU Risk Assessment Report, Tris(2-chloro-1-methylethyl) phosphate, TCPP (Draft). **2007b**; Available through ORATS (Online EUropean Risk Assessment Tracking System).

Finneran K.T., Lovley D.R. Anaerobic degradation of Methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA). Environ Sci Technol **2001**, 35, 1785-1790.

Fischer A. and Hahn C. Biotic and abiotic degradation behavior of ethylene glycol monomethyl ether (EGME). Water Res **2005**, 39, 2002-2007.

Flury M. and Wai N.N. Dyes as tracers for vadose zone hydrology, Rev Geophys **2003**, 41, 2-1 - 2-37.

Fries E. and Püttmann W. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). J Environ Monit **2003**, 5, 346-352.

Fruijtier-Pölloth C. Safety assessment on polyethelene glycols (PEGs) and their derivatives as used in cosmetic products. Toxicolgy **2005**, 214, 1-37.

Fuh C.B., Lai M., Tsai H.Y., Chang C.M. Impurity analysis of 1,4-dioxane in nonionic surfactants and cosmetics using headspace solid-phase micro-extraction coupled with gas chromatography and gas chromatography-mass spectrometry, Journal Chromatogr A **2005**, 1071, 141-145.

Fujiwara T., Tamada T., Kurata Y., Ono Y., Kose T., Ono Y., Nishimura F., Ohtoshi K. Investigation of 1,4-dioxane originating from incineration residues produced by incineration of municipal solid waste. Chemosphere **2008**, 71, 894-901.

Geiger H. and Becker K.H. Degradation mechanisms of dimethoxymethane and dimethoxyethane in the presence of NO_x. Atmos Environ **1999**, 33, 2883-2891.

Gelman Sciences. Information on the dioxane content of polyethylene glycol, raw materials and consumer products with cover letter dated 011789. **1989**. Submitted to U.S. Environmental Protection Agency under TSCA Section 8E. OTS0516624-1.

George J.D., Price C.J., Kimmel C.A., Marr M.C. The developmental toxicity of triethylene glycol dimethyl ether in mice. Fund. Appl. Toxicol. **1987**, 9, 173-181.

German Bioethanol Industry Association. Retrieved April 17, **2011**, from http://www.bdbe.de/branche/marktdaten/.

Grossmann D., Köser H., Kretschmer R., Porobin M. Treatment of diglyme containing wastewater by advanced oxidation – process design and optimisation. Water Sci Technol **2001**, 44, 287-293.

Guedez A.A., Frömmel S., Diehl P., Püttmann W. Occurrence and temporal variations of TMDD in the river Rhine, Germany. Environ Sci Pollut Res **2010**, 17, 321-330.

Harasimowicz M., Palige J., Chmielewski A.G. Odzyskiwanie mieszaniny eterow metylowych glikoli polietylenowych Genosorb ® ze sciekow metoda selektywnej osmozy odwroconej (SeIRO), Przem. Chem. **2005**, 84, 247-249.

Hardin B.D. Reproductive toxicity of the glycol ethers. Toxicology **1983**, 27, 91-102.

Hartung R. Health and environmental effects assessment for 1,4-dioxane. **1989**. Ann Arbor, Michigan: Gelman Sciences.

Heberer T., Mechlinski A., Fanck B., Knappe A., Massmann G., Pekdeger A., Fritz B. Field studies on the fate and transport of pharmaceutical residues in bank filtration. Ground Water Monit R **2004**, 24, 70-77.

Heisel M.P. and Belloni A.E. Options available in the Solinox vent gas purification process. Gas Sep Purif **1991**, 5, 111-113.

Herrero-Hernández E., Rodríguez-Gonzalo E., Andrades M.S., Sánchez-González S., Carabias-Martínez R. Occurrence of phenols and phenoxyacid herbicids in environmental waters using an imprinted polymer as a selective sorbent. Sci Total Environ **2013**, 454-455, 299-306.

Hoppe-Jones C., Oldham G., Drewes J.E. Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems. Water Res **2010**, 44, 4643-4659.

Howard P.H. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. **1990**, Lewis Publishers, Inc., Chelsea, MI, 216-221.

Inal F., Yetgin S., Aksu G.T., Simsek S., Sofuoglu A., Sofuoglu S.C. Activated carbon adsorption of fuel oxygenated MTBE and ETBE from water. Water Air Soil Pollut **2009**, 204, 155-163.

International Association of Waterworks in the Rhine Catchment Area. Donau-, Maas-, Rhein-Memorandum **2008**. Retrived: July 28, 2013, from www.riwa-rijn.org.

International Association of Waterworks in the Rhine Catchment Area. Online data of water quality: Aqualarm. Retrived: March 12, **2013**, from aqualarm.nl.

International Uniform Chemical Information Database. IUCLID. Retrieved February 15, **2011**, from http://iuclid.eu/.

Isaacson C., Mohr T.K.G., Field J.A. Quantitative determination of 1,4-dioxane and tetrahydrofuran in groundwater by solid phase extraction GC/MS/MS. Environ Sci Technol **2006**, 40, 7305-7311.

Junk G.A., Avery M.J., Richard J.J. Interferences in solid-phase extraction using C-18 bonded porous silica cartridges. Anal Chem **1988**, 60, 1347-1350.

Kameya T., Murayama T., Urano K., Kitano M. Biodegradation ranks of priority organic compounds under anaerobic conditions. Sci Total Environ **1995**, 170, 43-51.

Kasprzyk-Hordern B., Dinsdale R.M., Guwy A.J. The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. Water Res **2008**, 42, 3498-3518.

Katsoyiannis I.A., Canonica S., von Gunten U. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O_3/H_2O_2, UV/H_2O_2. Water Res **2011**, 45, 3811-3822.

Kawagoshi Y., Nakamura S., Fukunaga I. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. Chemosphere **2002**, 48, 219-225.

Kawai F. Microbial degradation of polyethers. Appl Microbiol Biotechnol **2002**, 58, 30-38.

Kawata K. and Tanabe A. Distribution and variation of 1,4-dioxane in water from Rivers in Niigata including the Shinano River. Bull Environ Contam Toxicol **2009**, 86, 673-677.

Kawata K., Ibaraki T., Tanabe A., Yasuhara A. Distribution of 1,4-dioxane and *N*,*N*-dimethylformamide in river water from Niigata, Japan. Bull Environ Contam Toxicol **2003**, 70, 876-882.

Kawata K., Ibarki T., Tanabe A., Yagoh H., Shinoda A., Suzuki H., Yasuhara A. Gas chromatographic- mass spectrometric determination of hydrophilic compounds in environmental water by solid phase extraction with activated carbon felt. J Chromatogr A **2001**, 911, 75-83.

Kegel F.S., Rietman B.M., Verliefde A.R. Reverse osmosis followed by activated carbon filtration for efficient removal of organic micropollutants from river bank filtrate. Water Sci Technol **2010**, 61, 2603-2610.

Keith L.H., Waters D.B. Compendium of safety data sheets for research and industrial chemicals. Part II. **1985**, VCH Publishers, Deerfield Beach, 726.

Kiker J.H., Connolly J.B., Murray W.A., Pearson S.C., Reed S.E. Ex-Situ wellhead treatment of 1,4-dioxane using fenton's reagent. Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy **2010**, 15, 210-226.

Kim S.D., Cho J., Kim I.S., Vanderford B.J., Snyder S.A. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res **2007**, 41, 1013-1021.

Kim Y.-M., Jeon J.-R., Murugesan K., Kim E.-J., Chang Y.-S. Biodegradation of 1,4-dioxane and transformation of related cyclic compounds by a newly isolated *Mycobacterium* sp. PH-06. Biodegradation **2009**, 20, 511-519.

Knepper T.P., Sacher F., Lange F.T., Brauch H.J., Karrenbrock F., Roerden O., Lindner K. Detection of polar organic substances relevant for drinking water. Waste Manage **1999**, 19, 77-99.

Konstantinou I.K., Hela D.G., Albanis T.A. The status of pesticide pollution in surface waters (rivers and lakes) in Greece. Part I. Review on occurrence and levels. Environ Pollut **2006**, 141, 555-570.

Kraybill H.F. Carcinogenesis induced by contaminants in potable water. Bull NY Acad Med **1978**, 54, 413-427.

Kuster M., Díaz-Cruz S., Rossel M., López de Alda M., Barceló D. Fate of selected pesticides, estrogens, progestogens and volatile organic compounds during artificial aquifer recharge using surface waters. Chemosphere **2010**, 79, 880-886.

Landesamt für Umwelt, Gesundheit und Verbraucherschutz. Hydrologischer Wochenberichte. Potsdam, **2012**. Retrieved October 22, 2012, http://www.luis.brandenburg.de/w/wochenberichte/W7100038/default.aspx.

Landesamt für Umwelt, Wasserwirtschaft, und Gewerbeaufsicht Rheinland-Pflaz. Rheinwasser-Untersuchungsstation Mainz-Wiesbaden. **2006**, Oppenheim, Germany.

Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg [LUBW]. Grundwasser-Überwachungsprogramm. **2010**. Retrieved August 18, 2013, from www.lubw.baden-wuerttemberg.de.

Landmeyer J.E., Chapelle F.H., Bradley P.M., Pankow J.F., Church C.D., Tratnyek P.G. Fate of MTBE relative to benzene in a gasoline contaminated aquifer (1993-98). Ground Water Monit R **1999**; 18, 93-102.

Lee J.-Y., Cheon J.-Y., Lee K.-K., Lee S.-Y., Lee M.-H. Factors affecting the distribution of hydrocarbon contaminants and hydrogeochemical parameters in a shallow sand aquifer. J Contam Hydrol **2001**, 50, 139-158.

Leisewitz A., Kruse H., Schramm E. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals - Vol. 1. Umweltbundesamt **2001**. Berlin, Germany.

Lesage S., Jackson R.E., Priddle M.W., Riemann P.G.. Occurrence and fate of organic solvent residues in anoxic groundwater at the Gloucester landfill, Canada. Environ Sci Technol **1990**, 24, 559-566.

Liang L., Dickson J.M., Jiang J., Brook M.A. Pervapoation of 1,2-dimethoxyethane from aqueous solutions by crosslined oligosilylstyrene-poly(dimethylsiloxane) composite membranes. J Appl Polym Sci **2004**, 92, 2284-2294.

Loos R., Gawlik B.M., Locoro G., Rimaviciute E., Contini S., Bidoglio G. EU-wide survey of polar organic pollutants in European river waters. Environ Pollut **2009**, 157, 561-568.

Luckas S. and Diehl P. Optimierung der Abflussfaktoren für die Berechnung der Konzentrationen und Transporte an der messstelle Worms. **2000**, unpublished report of Rhein Water Control Station Worms (http://www.rheinguetestation.de/).

Massmann G. Infiltration of river water into the groundwater: Investigations and modeling of hydraulic and geochemical processes in the Oderbruch aquifer, Germany [dissertation]. Berlin, Germany: Free University Berlin; **2002**.

Massmann G., Pekdeger A., Merz C. Redox processes in the Oderbruch polder groundwater flow system in Germany. Appl Geochem **2004**, 19, 863-886.

Massmann G., Sültenfuß J., Pekdeger A. Analysis of long-term dispersion in a river-charged aquifer using tritium/helium date. Water Resour Res **2009**, 45, W02431.

Massmann G., Tichomirowa M., Merz C., Pekdeger A. Sulfide oxidation and sulfate reduction in a shallow ground-water system (Oderbruch Aquifer, Germany). J Hydrol **2003**, 278, 231-243.

Masuda H., McClay K., Steffan R.J., Zylstra G.J. Biodegradation of tetrahydrofuran and 1,4-dioxane by soluble diiron Monooxygenase in *Pseudonocardia* sp. Strain ENV478. J Mol Microbiol Biotechnol **2012**, 22, 312-316.

Merz C., Schuhmacher P., Winkler A., Pekdeger A. Identification and regional quantification of hydrochemical processes at the contact zone between anoxic groundwater and surface water in poldered floodplains (Oderbruch polder, Germany). Appl Geochem **2005**, 20, 241-254.

Mohr T.K.G. Environmental Investigation and Remediation: 1,4-Dioxane and other Solvent Stabilizer. **2010**, Boca Raton, FL, CRC Press.

Morgenstern P., Versteegh A.F.M., de Korte G.A.L, Hoogerbrugge, R., Mooibroek, D., Bannink, A., Hogendoorn, E.A. Survey of the occurrence of residues of methyl *tertriary* butyl ether (MTBE) in Dutch drinking water sources and drinking water. J Environ Monit **2003**, 5, 885-890.

Mormille M.R., Liu S., Sulfita J.M. Anaerobic biodegradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions. Environ Sci Technol **1994**, 28, 1727-32.

Mudelsee M., Börngen M., Tetzlaff G., Grünewald U. No upward trend in the occurrence of extreme floods in central Europe. Nature **2003**, 425, 166-168.

Muir D.C.G. The Handbook of Environmental Chemistry - Volume 3 Part C. Berlin: Springer, **1984**.

National Industrial Chemicals Notification and Assessment Scheme. 1,4-dioxane – priority existing chemical No.7, full public report. **1998.** Retrived May 4, 2011, from htpp://www.nicnas.gov.au/publications/car/pec/pec7/Pec7_full_report_pdf.pdf.

Noordsij A., Puyker L.M.,van der Gaag M.A. The quality of drinking water prepared from bank-filtered river water in the Netherlands. Sci Total Environ **1985**, 47, 273-292.

Nowotny N., Epp B., von Sonntag C., Fahlenkamp, H. Quantification and modeling of the elimination behavior of ecologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon. Environ Sci Technol **2007**, 41, 2050-2055.

Ortega J.A.T. Sulfonation/Sulfation processing technology for anionic surfactant manufacture, Advances in Chemical Engineering, **2012**, Dr. Zeeshan Nawaz (Ed.), ISBN: 978-958-51-0392-9, InTech. Available from: www.intechopen.com.

Park Y.M., Pyo H., Park S.J., Park S.K. Development of the analytical method for 1,4-dioxane in water by liquid-liquid extraction. Anal Chim Acta **2005**, 48, 109-115.

Paxéus N. Organic compounds in municipal landfill leachates. Water Sci Technol **2000**, 4, 323-333.

Peters N.E., Ratcliffe E.B., Tranter M. Tracing solute mobility at the Panola Mountain Research Watershed, Georgia, USA: variations in Na^+, Cl^-, and H_4SiO_4 concentrations. Proceedings of the HeadWater´98 Conference, **1998** April, Marano, Italy. IAHS Publ. no. 248.

Pitt R., Clark S., Field R. Groundwater contamination potential from stormwater infiltration practices. Urban Water **1999**, 1, 217-236.

Popoola A.V. Mechanism of the reaction involving the formation of dioxane byproduct during the production of poly(ethylene terephthalate). J Appl Polym Sci **1991**, 43, 1875-1877.

Rastogi S.C. Headspace analysis of 1,4-dioxane in products containing polyethoxylated surfactants by GC/MS. Chromatographia **1990**, 29, 441-445.

Rauch-Williams T., Hoppe-Jones C., Drewes J.E. The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. Water Res **2010,** 44, 449-460.

Reemtsma T., Quintana J.B., Rodil R., García-López M., Rodriguez, I. Organophosphorus flame retardants and plasticizers in water and air - I. Occurrence and fate. TrAC-Trends Anal Chem **2008**, 27, 727-737.

Regnery J., Püttmann W. Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. CLEAN - Soil, Air, Water **2009**, 37, 334-342.

Regnery J., Püttmann W. Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. Chemosphere **2010**, 78, 958-964.

Remier N. German Biofuels Policy and bioethanol market. German Bioethanol Industry Association, **2012**. Available at: http://www.ahkzakk.com/fileadmin/ahk_zakk/Events/Delegationsreise_EE_2012/Presentaciones_Infotag/Bioethanol.pdf.

Rhine Water Works (RIWA). Jahresbericht **2005**, Der Rhein. The Netherlands. Retrived May 22, 2013, from http://www.riwa-rijn.org/uploads/tx_deriwa/139_JR_2005_du.pdf.

Rhine Water Works. Jahresbericht **2006**, Der Rhein. The Netherlands. Retrived May 22, 2013, from http://www.riwa-rijn.org/uploads/tx_deriwa/149_JR_2006_du.pdf.

Rhine Water Works. Jahresbericht **2011**, Der Rhein. The Netherlands. Retrived May 11, 2012, from http://www.riwa-rijn.org.

Rhine Water Works. Jahresbericht **2012**, Der Rein. The Netherlands. Retrived May 22, 2013, fromhttp://www.riwa-rijn.org/uploads/tx_deriwa/RIWA0041_jaarrapport_dui-Internet_2012.pdf.

Robinson J.J. and Ciurczak E.W. Direct gas chromatographic determination of 1,4-dioane in ethoxylated surfactants. J Soc Cosmet Chem **1980**, 31, 329-337.

Romero J., Ventura F., Caixach J. Identification of 1,3-dioxanes and 1,3 dioxolanes as malodorous compounds at trace levels in river water, groundwater, and tap water. Environ Sci Technol **1998**, 32, 206-216.

Rosell M., Lacorte S., Ginebreda A., Barceló. Simultaneous determination of methyl *tert*-butyl ether and its degradation products, other gasoline oxygenates and benzene, toluene, ethylbenzene and xylenes in Catalonian groundwater by purge-and-trap gas chromatography-mass spectrometry. J Chromatogr A **2003**, 995, 171-184.

Roy D., Anagnostu, G., Chaphalkar, P. Biodegradation of dioxane and diglyme in industrial waste. J Environ Sci Health **1994**, A29, 129-147.

Sacher F., Ehmann M., Gabriel S., Graf C., Brauch H.J. Pharmaceutical residues in the river Rhine – results of a one-decade monitoring programme. J Environ Monitor **2008**, 10, 664-670.

Saeger V.W., Hicks O., Kaley R.G., Michael P.R., Mieure J.P., Tucker E.S. Environmental fate of selected phosphate esters. Environ Sci Technol **1979**, 13, 840-844.

Safarzadeh-Amiri A., Bolton J.R., Carter S.R.. Ferrioxalate-mediated photodegradation of organic pollutants in contaminated water. Water Res **1997**, 31, 787-798.

Scalia S. Reversed-phase high-performance liquid chromatographic method for the assay of 1,4-dioane in sulphated polyoxyethylene alcohol surfactants. J Pharm Biomed Anal **1990**, 8, 867-870.

Scheirs J., Long T.E.. Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters. **2003**, Wiley, ISBN: 978-0-471-49856-8.

Schmidt C.K. Datenbank zum Verhalten organischer Spurenstoffe bei der Uferfiltration. DVGW-Technologiezentrum Wasser **2005**, Karlsruhe, Germany.

Schmidt C.K., Lange, F.T., Brauch, H.J., Kühn, W. Experiences with riverbank filtration and infiltration in Germany. DVGW- Water Technology Center **2003** (TZW).

Schriks M., Heringa M.B., van der Kooi M.M.E., de Voogt P., van Wezel A.P. Toxicological relevance of emerging contaminants for drinking water quality. Water Res **2010**, 44, 461-476.

Schroeder G. Środowisko i przemysł (Environment and industry). Cursiva, **2010**, ISBN: 978-83-62108-05-3.

Schwarzenbach R.P., Giger W., Hoehn E., Schneider J.K. Behavior of organic compounds during infiltration of river water to groundwater. Field studies. Environ Sci Technol **1983**, 17, 472-479.

Schwetz B.A., Price C.J., George J.D., Kimmel C.A., Morrissey R.E., Marr M.C. The developmental toxicity of diethylene and triethylene glycol dimethyl ethers in rabbits. Fund Appl Toxicol **1992**, 19, 238-245.

Sczczęśniak S. Metoda Solinox alternatywą usuwania SO_2 z gazów odlotowych. In: Grzesiak P.; Schroeder G.; Pruszyński S. Kwas Siarkowy – Wczoraj – Dziś – Jutro. IOR Poznań, **2000**, ISBN: 83-913860-0-7, 335-341.

Sei K., Kakinoki T., Inoue D., Soda S., Fujita M., Ike M. Evaluation of the biodegradation potential of 1,4-dioxane in river, soil and activated sludge samples. Biodegradation **2010**, 21, 585-591.

Shen W., Chen H., Pan S. Anaerobic biodegradation of 1,4-dioxane by sludge enriched with iron-reducing microorganisms. Bioresource Technol **2008**, 99, 2483-2487.

Shirey R.E., Linton C.M. The extraction and analysis of 1,4-dioxane from water using solid-phase microextraction coupled with gas chromatography and gas chromatography-mass spectrometry. J Chromatogr Sci **2006**, 44, 444-450.

Skutlarek D., Exner M., Färber H. Perfluorinated surfactants in surface and drinking water. Environ Sci Pollut Res **2006**, 13, 299-307.

So M.H., Han J.S., Han T.H., Seo J.W., Kim S.G. Decomposition of 1,4-dioxane by photo-Fenton oxidation coupled with activated sludge in a polyester manufacturing process. Water Sci Technol **2009**, 59, 1003-1009.

Sporer J. The Linde Solinox process: gypsum-free flue-gas desulphurization. Gas Sep Purif **1992**, 6, 133-140.

Stapleton H.M., Sharma S., Getzinger G., Lee Ferguson P., Gabriel M., Webster T.F., Blum A. Novel and high volume use flame retardants in US coches reflective of the 2005 PentaBDE phase out. Environ Sci Technol **2012**, 46, 13432-13439.

Stefan M.I. and Bolton J.R. Mechanism of the degradation of 1,4-dioxane in dilute aqueous solution using the UV/hydrogen peroxide process. Environ Sci Technol **1998**, 32, 1588-1595.

Stepien D.K. and Püttmann W. Simultaneous determination of six hydrophilic ethers at trace levels using coconut charcoal adsorbent and gas chromatography/mass spectrometry. Anal Bioanal Chem **2013**, 405, 1743-1751.

Stepien D.K., Regnery J., Merz C., Püttmann W. Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany. Sci Total Environ **2013**, 458-460, 150-159.

Stupp D., Gass M., Leiteritz H., Pijls C., Thornton S., Smith J., Dunk M., Grosjean T., den Haan K., Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment, Report no. 4/12, CONCAWE, Brussels, June **2012**.

Stuyfzand P.J., Segers W., van Rooijen N. Behavior of pharmaceuticals and other emerging pollutants in various artificial recharge systems in the Netherlands. Management of aquifer recharge for sustainability, Proc. ISMAr-6, **2007**, 231-245.

Suh J.H. and Mohseni M. A study on the relationship between biodegradability enhancement and oxidation of 1,4-dioxane using ozone and hydrogen peroxide. Water Res **2004**, 38, 2596-2604.

Sültenfuß J. and Massmann G. Dating with the 3He-tritium-method: An example of bank filtration in the Oderbruch region. Grundwasser **2004**, 9, 221-234.

Sun B., Ko K., Ramsay J.A. Biodegradation of 1,4-dioxane by a *Flavobacterium*. Biodegradation **2011**, 22, 651-659.

Tanabe A., Tsuchida Y., Ibaraki T., Kawata K. Impact of 1,4-dioxane from domestic effluent on the Agano and Shinano Rivers, Japan. Bull Environ Contam Toxicol **2006**, 76, 44-51.

Tosaki Y., Tase N., Massmann G., Nagashima Y., Seki R., Takahashi T., et al. Application of 36Cl as a dating tool for modern groundwater. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **2007**, 259, 479-485.

Tufenkij N., Ryan J.N., Elimelech, M. The promise of bank filtration. Environ Sci Technol **2002**, 423A-428A.

U.S. Department of Defense. Environmental Security Technology Certification Program, Strategic Environmental Research and Development Program, Final Report: ER-1422: Biodegradation of 1,4-dioxane. **2007**.

U.S. Environmental Protection Agency. EPA Report 600/R-08/101, **2008**, Office of Research and Development, Cincinnati, Ohio.

U.S. Environmental Protection Agency. Treatment technologies for 1,4-dioxane: fundamentals and field applications, Office of Solid Waste and Emergency Response, EPA-542-R-06-009 **2009**.

U.S. Environmental Protection Agency. Treating contaminants of emerging concern. **2010**, EPA-820-R-10-002, Washington DC.

U.S. Environmental Protection Agency. Glymes; proposed significant new use rule EPA 40 CFR Part 721. **2011**, Federal Registry,76, 133: 40850-40860.

U.S. Environmental Protection Agency.Title 40: protection of environment; part 136 – guidelines establishing test procedures for the analysis of pollutants; Appendix B to Part 136 - definition and procedure for the determination of the method detection limit – revision 1.1, **2011a**.

U.S. Environmental Protection Agency. Estimation Program Interface Suite^{TM} for Microsoft$^{®}$ Windows, v 4.10. United States Environmental Protection Agency, Washington, DC, USA **2011b**.

Umwelbundesamt. Bewertung der Anwesenheit teil- oder nicht bewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht. Empfehlung des Umweltbundesamtes nach Anhö-rung der Trinkwasserkommission beim Umweltbundesamt. Bundesgesundheitsbl – Ge-sundheitsforsch – Gesundheitsschutz **2003**, 46, 249–251.

Vainberg S., McClay K., Masuda H., Root D., Condee C., Zylstra G.J., Steffan R.J. Biodegradation of ether pollutants by *Pseudonocardia* sp. Strain ENV478. Appl Environ Microb **2006**, 72, 5218-5224.

van Steel L., Leonards P., van Loon W., Hendriks A., Maas J., Struijs J., Brinkman U. Use of semi-permeable membrane devices and solid-phase extraction for the wide-range screening of microcontaminants in surface watr by GC-AED/MS. Water Res **2002**, 36, 4455-4470.

van Wezel A., Puijker L., Vink C., Versteegh A., de Voogt P. Odor and flavor thresholds of gasoline additives (MTBE, ETBE and TAME) and their occurrence in Dutch drinking water collection areas. Chemosphere **2009**, 76, 672-676.

Verbruggen E.M.J., Rila J.P., Traas T.P., Posthuma-Doodeman C.J.A.M., Posthumus, R. Environmental Risk Limits for Several Phosphate Esters with Possible Application as Flame

Retardant. National Institute for Public Health and the Environment **2005**, Bilthoven, Netherlands.

Verschueren K. Handbook of Environmental Data on Organic Chemicals, 2nd Ed. **1983**, VanNostrand Reinhold Co., New York, 578-580.

Wagner J., Porter E., Collins E., Treacy J. Sidebottom H. Mechanisms of the chlorine atom initiated oxidation of dimethoxymethane and 1,2-dimethoxyethane in the presence of NO_x. Chemosphere **1999**, 38, 1997-1204.

Wiese B., Massmann G., Jekel M., Heberer T., Dünnbier U., Orlikowski D., Grützmacher G. Removal kinetics of organic compounds and sum parameters under field conditions for managed aquifer recharge. Water Res **2011**, 45, 4939-4950.

Wirtz F. Danube, Meuse and Rhine MEMORANDUM 2008. Environ Sci Pollut Res **2009**, 16 (Suppl 1), S112-S115.

World Health Organization. Diethylene glycol dimethyl ether. Technical report. Geneva. **2002**.

World Health Organization. Flame Retardants: Tris(2-butoxyethyl) phosphate, Tris(2-ethylhexyl) phosphate and Tetrakis(hydroxymethyl) phosphonium salts. Environmental Health Criteria 218, **2000**, Geneva, Switzerland.

Yasuhara A. and Tanaka Y. Elution of 1,4-dioxane from waste landfill sites, Bull Environ Contam Toxicol **2003**, 71, 641-646.

Zenker M.J., Border R.C., Barlaz M.A. Occurrence and treatment of 1,4-dioxane in aqueous environments. Environ Eng Sci **2003**, 20, 423-432.

Appendix

TABLE A. 1 Stability of ethers in ultrapure water (*n* = *5*) and the Main River samples and the percent difference in concentration between day 0 and 9.

	Concentration (µg L^{-1})				
	Ultrapure water, *n* = *5*				
Analyte	Day 0	Day 2	Day 5	Day 9	% Difference
EtBe	0.901	0.830	0.813	0.803	10.90%
Monoglyme	0.983	0.947	0.946	0.891	5.90%
1,4-dioxane	0.959	0.915	0.884	0.851	11.30%
Diglyme	1.029	1.011	0.999	0.983	4.47%
Triglyme	0.947	0.856	0.835	0.830	12.40%
Tetraglyme	0.965	0.889	0.868	0.836	13.40%
	Surface water (Main River), *n* = *2*				% Difference
EtBe	0.901	0.857	0.855	0.722	19.9 %
Monoglyme	1.010	0.991	0.948	0.953	6.13 %
1,4-dioxane	1.001	0.950	0.874	0.777	22.4 %
Diglyme	1.064	1.020	0.983	0.982	7.71 %
Triglyme	0.927	0.840	0.833	0.790	14.8 %
Tetraglyme	1.028	0.933	0.890	0.811	21.1 %

TABLE A. 2 Stability of ethers in dichloromethane extracts over 13-day period and percent difference in concentration between day 0 and 13.

	Concentration (µg L^{-1}), *n* = *7*					
Analyte	Day 0	Day 2	Day 5	Day 9	Day 13	% Difference
EtBe	1.014	0.888	0.908	0.832	0.862	9.26%
Monoglyme	1.102	0.961	1.018	1.001	1.002	2.12%
1,4-dioxane	1.041	0.971	0.894	0.966	0.971	8.21%
Diglyme	1.05	1.039	0.983	0.824	0.79	18.20%
Triglyme	0.949	0.942	0.885	0.793	0.733	13.50%
Tetraglyme	0.989	0.983	0.902	0.932	0.939	6.28%

TABLE A. 3 Concentration of redox relevant parameters with standard deviation in the Oder River (n = 1) and six deep groundwater wells (*n* = *3*): redox potential (Eh), dissolved organic carbon (DOC), pH, conductivity (K), oxygen (O_2), nitrate (NO_3^-), ferrous iron (Fe(II)) and sulfate (SO_4^{2}).

Sample ID	Distance [m]	pH	Eh [mV]	K [mV]	O_2 [mg L^{-1}]	NO_3^- [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	DOC [mg L^{-1}]	Fe(II) [mg L^{-1}]
Oder River	0	7.66	242.5	709	15.080	11.55	83.50	7.59	0.01
6/99-D	138	7.62±0.254	78.17±58.75	733±37.6	0.093±0.035	1.033±0.112	75.5±1.47	6.27±0.776	0.413±0.219
9560-D	604	7.53±0.267	55.00±47.44	766±33.7	0.177±0.074	0.960±0.020	82.8±4.12	4.15±0.348	1.540±0.121
6/05-D	1150	7.54±0.262	65.10±26.73	792±7.2	0.117±0.031	1.039±0.109	89.4±2.30	4.40±0.719	1.747±0.352
4/04-D	2560	6.90±0.266	73.47±28.2	620±12.9	0.133±0.050	1.007±0.090	96.3±13.77	5.34±0.819	11.233±2.887
3/05-D	2980	6.97±0.252	65.57±39.01	709±11.4	0.160±0.060	0.950±0.000	127.4±6.04	6.74±1.734	13.640±2.944
2144-D	3434	6.89±0.241	79.67±24.17	601±2.5	0.147±0.168	1.040±0.090	49.9±3.49	8.41±0.537	12.360±3.429

TABLE A. 4 Discharge ($m^3\ s^{-1}$) and water level (m) of the Oder River during sampling campaigns.

Sampling Date	Water level (m)	Discharge ($m^3\ s^{-1}$)
27-Oct-09	296	397
10-Mar-11	438	813
29-Mar-12	417	740
24-May-12	298	381

TABLE A. 5 Concentration of chloride ($mg\ L^{-1}$), 1,4-dioxane and tetraglyme ($ng\ L^{-1}$) in the Oder River and deep groundwater wells during four sampling campaigns.

Sampling Date	Sample ID	Chloride ($mg\ L^{-1}$)	Tetraglyme ($ng\ L^{-1}$)	1,4-Dioxane ($ng\ L^{-1}$)
27-Oct-09	Oder	132.0	1260	n.a.
10-Mar-11		81.7	273	n.a.
29-Mar-12		93.8	1433	1610
24-May-12		163.0	1576	3290
27-Oct-09	6/99 T	128.9	1230	n.a.
10-Mar-11		86.9	339	n.a.
29-Mar-12		106.0	455	1340
24-May-12		111.0	496	1060
27-Oct-09	9560T	115.2	849	n.a.
10-Mar-11		115.0	369	n.a.
29-Mar-12		104.0	520	1020
24-May-12		98.0	630	901
27-Oct-09	6/05T	109.8	442	n.a.
10-Mar-11		114.0	212	n.a.
29-Mar-12		116.0	565	1630
24-May-12		116.0	741	1129
29-Mar-12	4/05 T	55.6	n.d.	208
24-May-12		57.8	n.d.	219

n.d. - not detected

n.a. - not analyzed

TABLE A. 6 Influent and effluent concentrations of 1,4-dioxane in µg L^{-1} in STP A, B, and C.

	STP A	STP B	STP D
Sampling period	10.12.12-16.12.12	13.11.12-20.11.12	08.07.13-14.07.13
Influent	0.272	0.401	0.499
	0.227	0.295	0.593
	0.213	0.353	0.558
	0.269	0.395	0.568
	0.262	0.369	0.510
	0.303	0.210	0.372
	0.238	0.355	0.512
		0.347	
Effluent	0.261	0.408	0.467
	0.248	0.402	0.246
	0.237	0.355	0.393
	0.274	0.331	0.500
	0.278	0.382	0.420
	0.339	0.306	0.235
	0.292	0.367	0.273
		0.306	

TABLE A. 7 1,4-Dioxane concentrations (µg L^{-1}) in STP C during two sampling campaigns.

Sampling period	Influent	1° Treatment	2° Treatment	Effluent
27.11.12-03.12.12	2.355	n.a.	n.a.	31.9
	0.825	n.a.	n.a.	59.7
	1.030	n.a.	n.a.	80.9
	0.743	n.a.	n.a.	60.7
	0.595	n.a.	n.a.	23.6
	0.631	n.a.	n.a.	14.2
	0.495	n.a.	n.a.	12.5
17.01.13-22.01.13	0.736	9.11	8.36	108.0
	0.779	7.27	7.97	96.7
	1.159	6.89	7.56	96.8
	0.609	5.31	5.33	57.7
	0.407	1.55	1.24	50.0
	0.710	5.18	4.46	49.9
	0.598	7.53	5.69	129.0

n.a. – not analyzed

TABLE A. 8 Concentration of 1,4-dioxane (ng L^{-1}) on the left (MWL1) and on the right (MWL4) side of the Rhine River during a two week study at the Rhine Water Control Station Worms, Germany and the average daily river discharge (m^3 s^{-1}).

Sampling date	MWL1 (ng L^{-1})	MWL4 (ng L^{-1})	Discharge (m^3 s^{-1})	Load MWL1 (kg d^{-1})	Load MWL2 (kg d^{-1})
20-Aug-12	1272	807	892	98.1	62.2
21-Aug-12	1384	374	886	105.9	28.6
22-Aug-12	666	596	898	51.7	46.2
23-Aug-12	1346	737	909	105.7	57.9
24-Aug-12	2238	1208	918	177.6	95.8
25-Aug-12	1182	853	951	97.1	70.1
26-Aug-12	815	664	994	70.0	57.0
27-Aug-12	442	249	1079	41.2	23.2
28-Aug-12	555	621	1113	53.4	59.7
29-Aug-12	702	692	1083	65.7	64.7
30-Aug-12	590	685	1056	53.8	62.5
31-Aug-12	479	630	1089	45.1	59.3
1-Sep-12	434	582	1248	46.8	62.7
2-Sep-12	365	376	1541	48.6	50.1

TABLE A. 9 Monthly concentrations of 1,4-dioxane in 2012 at the monitoring station Lobith, Germany with the discharge values (m^3 s^{-1}). (*Source*: RIWA-database Nieuwegein).

Sampling month	1,4-dioxane (ng L^{-1})	Discharge (m^3 s^{-1})
Jan-12	BDL	5982
Feb-12	1100	1880
Mar-12	1700	1709
Apr-12	1200	1352
May-12	950	1836
Jun-12	640	2213
Jul-12	1300	1806
Aug-12	1100	1224
Sep-12	1600	1493
Oct-12	790	2899
Nov-12	790	2553
Dec-12	1000	2258

TABLE A. 10 Concentrations and loads of 1,4-dioxane in the Oder, Rhine, and Main Rivers.

Sample ID	1,4-dioxane ng L^{-1}	Load kg d^{-1}	Sample ID	1,4-dioxane ng L^{-1}	Load kg d^{-1}
Od1	891		Od28	309	
Od2	782		Od29	305	6.93
Od3	793	55.2	Od30	230	5.78
Od4	797	55.5	Od31	278	
Od5	1610	51.5	Rh2	856	102
Od6	1851	68.3	Rh3	685	81.7
Od7	1457		Rh4	234	52
Od8	861	7.24	Rh5	452	
Od9	806		Rh6	470	145
Od10	783	5.9	Rh7	429	
Od11	727	5.18	Rh8	391	118
Od12	1055		Rh9	421	132
Od13	1541		Rh10	352	
Od14	934	8.4	Rh11	380	120
Od15	901	8.25	Rh12	611	197
Od16	672		Rh13	554	
Od17	859		Rh14	498	159
Od18	176		Rh15	471	153
Od19	217		Ma1	117	1.57
Od20	184		Ma2	308	4.15
Od21	184		Ma3	363	4.89
Od22	226		Ma4	624	8.41
Od23	403		Ma5	542	7.31
Od24	280		Ma6	750	10.1
Od25	447		Ma7	680	9.17
Od26	230	5.62	Ma8	526	6.63
Od27	298				

TABLE A. 11 Detected concentrations (μg L^{-1}) of diglyme, triglyme and tetraglyme on the left and on the right bank of the Oder River.

Sample	*Left*			Sample	*Right*		
ID	Diglyme	Triglyme	Tetraglyme	ID	Diglyme	Triglyme	Tetraglyme
OD-1	n.d.	n.d.	0.142	OD-1	n.d.	n.d.	0.112
OD-2	n.d.	n.d.	0.607	OD-2	n.d.	n.d.	0.308
OD-4	n.d.	n.d.	0.049	OD-3	n.d.	n.d.	0.047
OD-5	n.d.	n.d.	0.041	OD-5	n.d.	n.d.	0.035
OD-6	n.d.	n.d.	0.030	OD-6	n.d.	n.d.	0.043
OD-7	n.d.	n.d.	0.049	OD-8	n.d.	n.d.	0.112
OD-11	n.d.	n.d.	0.049	OD-9	n.d.	n.d.	0.065
OD-12	n.d.	n.d.	0.056	OD-10	n.d.	n.d.	0.098
OD-13	n.d.	n.d.	0.085	OD-12	n.d.	n.d.	0.045
OD-14	n.d.	0.461	1.147	OD-13	n.d.	n.d.	0.084
OD-15	0.055	0.247	3.270	OD-14	n.d.	0.272	0.581
OD-16	n.d.	0.162	1.165	OD-15	0.057	0.323	4.014
OD-17	n.d.	0.596	14.848	OD-16	n.d.	0.256	1.165
OD-18	n.d.	0.324	2.133	OD-17	n.d.	0.570	14.388
OD-19	n.d.	1.013	28.190	OD-20	n.d.	0.253	1.737
OD-20	n.d.	0.325	2.214	OD-21	n.d.	0.987	28.530
OD-21	n.d.	0.944	27.230	OD-22	n.d.	0.148	0.286
OD-22	n.d.	0.143	0.296	OD-23	n.d.	0.119	0.326
OD-26	n.d.	0.122	0.604	OD-24	n.d.	0.074	0.214
OD-27	0.073	0.426	1.620	OD-25	n.d.	0.070	0.290
OD-28	0.050	0.536	1.620	OD-33	0.037	0.049	0.258
OD-29	0.076	0.209	1.437	OD-36	0.031	0.077	0.402
Od-30	0.062	0.528	1.470	OD-37	0.034	0.066	0.315
OD-31	0.074	0.475	1.730				
OD-32	0.065	0.200	1.387				
OD-34	0.071	0.163	0.857				
OD-35	0.061	0.099	0.527				

n.d. – not detected

TABLE A. 12 Load of diglyme, triglyme and tetraglyme (kg d^{-1}) at sampling locations where information on discharge was available.

Sample ID	Diglyme kg d^{-1}	Triglyme kg d^{-1}	Tetraglyme kg d^{-1}
OD-35	2.01	3.26	17.35
OD-34	2.34	5.37	28.21
OD-32	2.12	6.51	45.18
OD-29	2.38	6.54	44.94
OD-30	4.32	36.77	102.37
OD-31	5.15	33.08	120.47
OD-24	n.d.	0.62	1.79
OD-22	n.d.	1.09	2.19
OD-21	n.d.	23.61	681.70
OD-20	n.d.	2.05	14.00
OD-15	1.28	6.48	82.80
OD-14	n.d.	3.29	10.31
OD-13	n.d.	n.d.	2.13
OD-9	n.d.	2.44	7.76
KW-1	4.10	9.24	61.43

n.d. – not detected

TABLE A. 13 Concentration and load of diglyme, triglyme and tetraglyme in the three samples obtained from the wastewater treatment plant in Legnica,PL.

	Sample-1	Sample-2	Sample-3
	Concentration (µg L^{-1})		
Diglyme	13.6	1.02	1692
Triglyme	228	63	12600
Tetraglyme	6340	809	190630
	Load (kg d^{-1})		
Diglyme	0.05	0.004	6.43
Triglyme	0.87	0.24	47.90
Tetraglyme	24.1	3.08	724.7

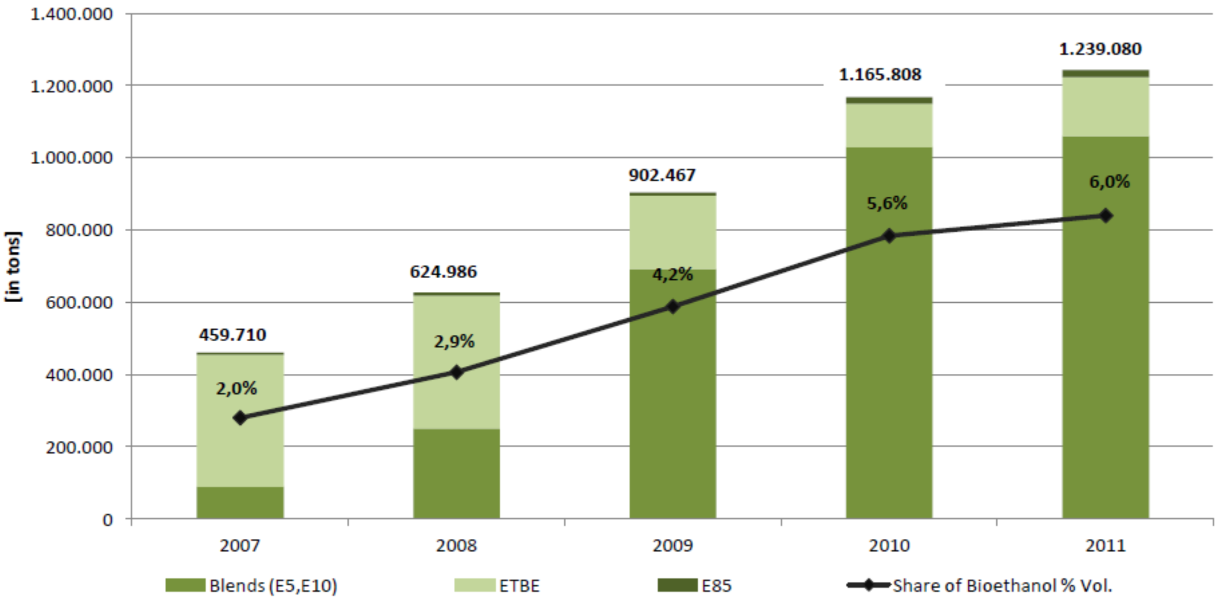
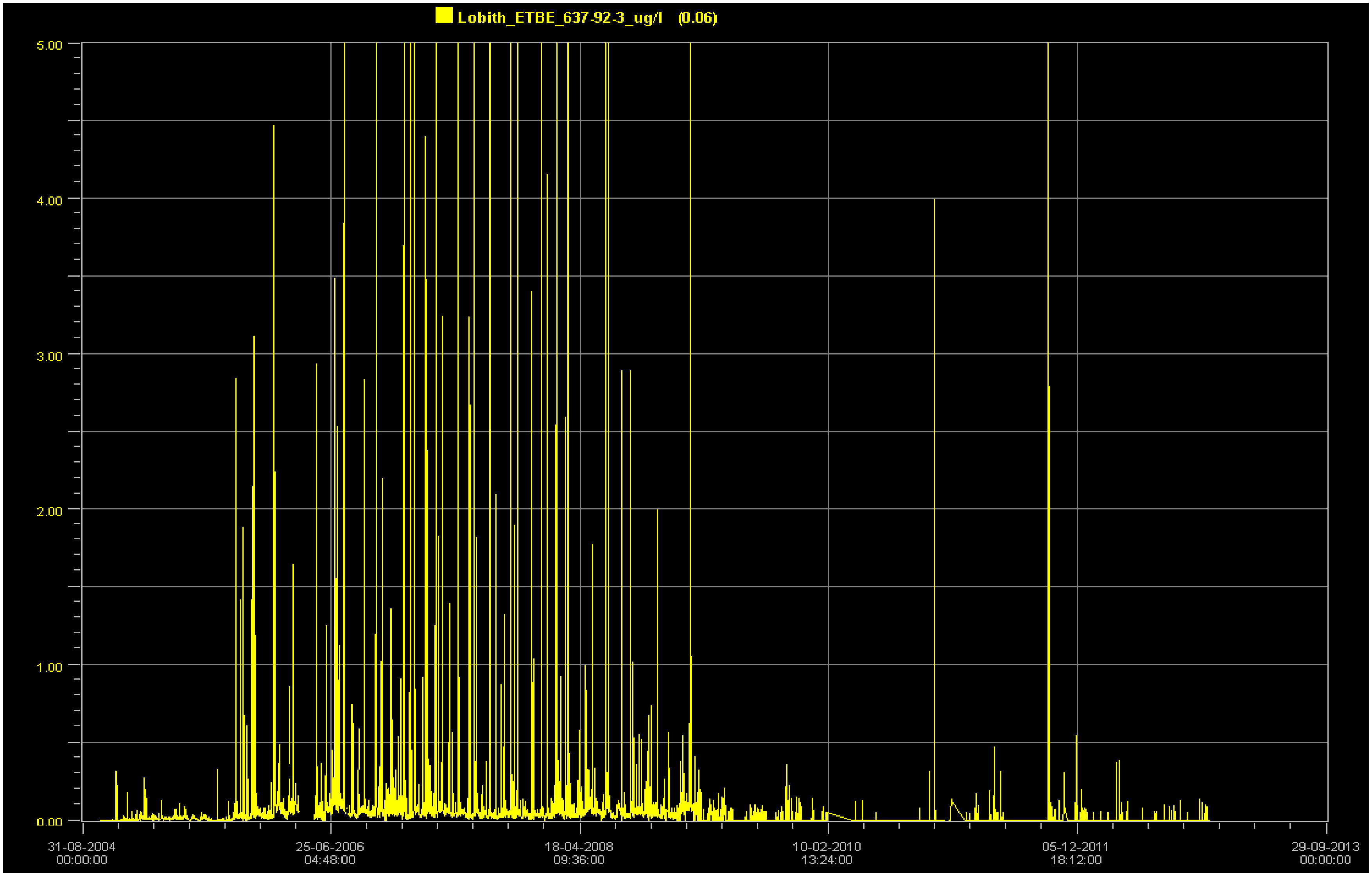


FIGURE A. 1 Consumption of bioethanol in Germany from 2007 to 2011 (*Source:* German Bioethanol Industry Association). The amount of bioethanol used for production of ETBE has decreased throughout the years.

a)


Lobith_ETBE_637-92-3_ug/l (0.06)
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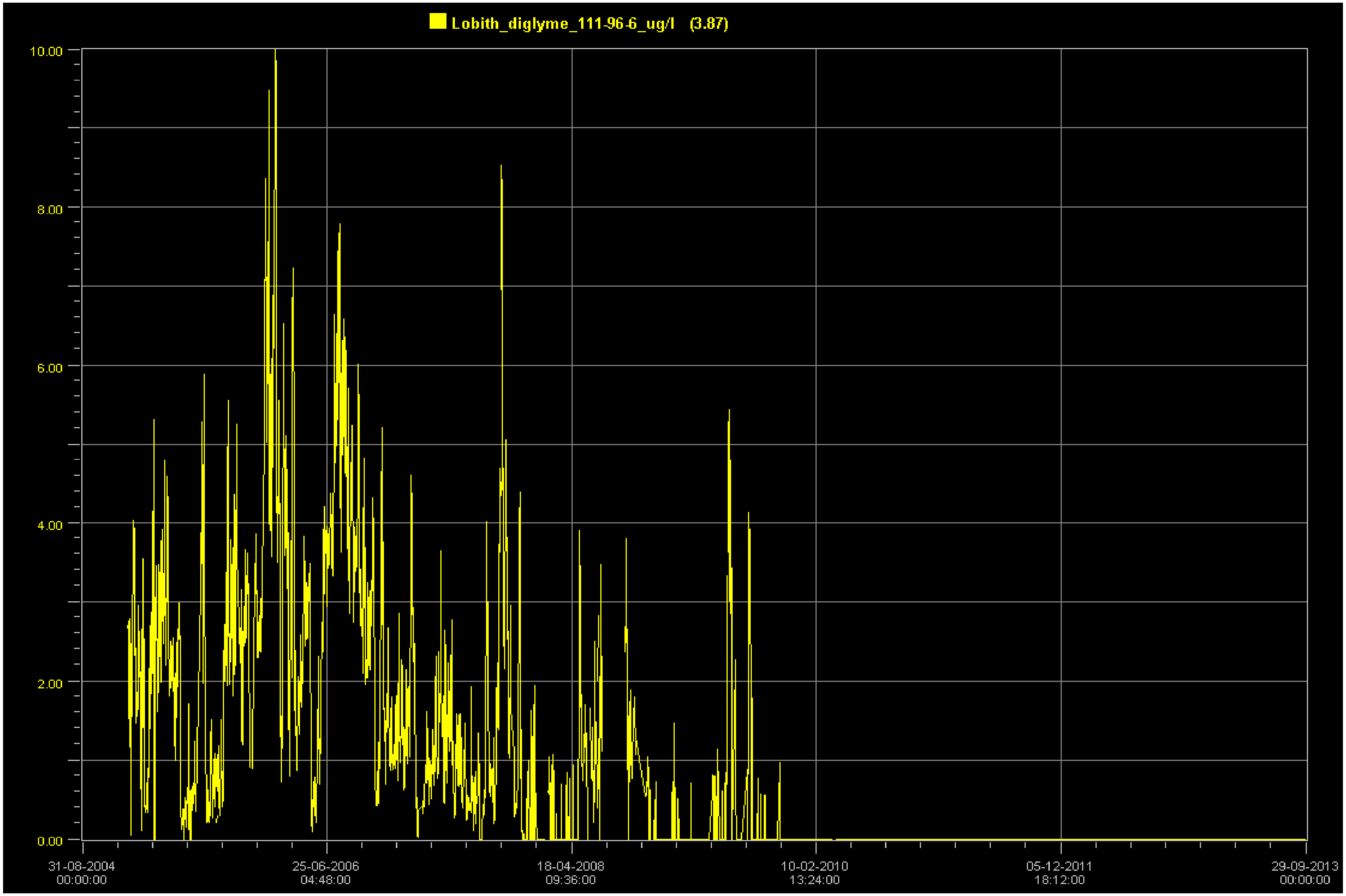
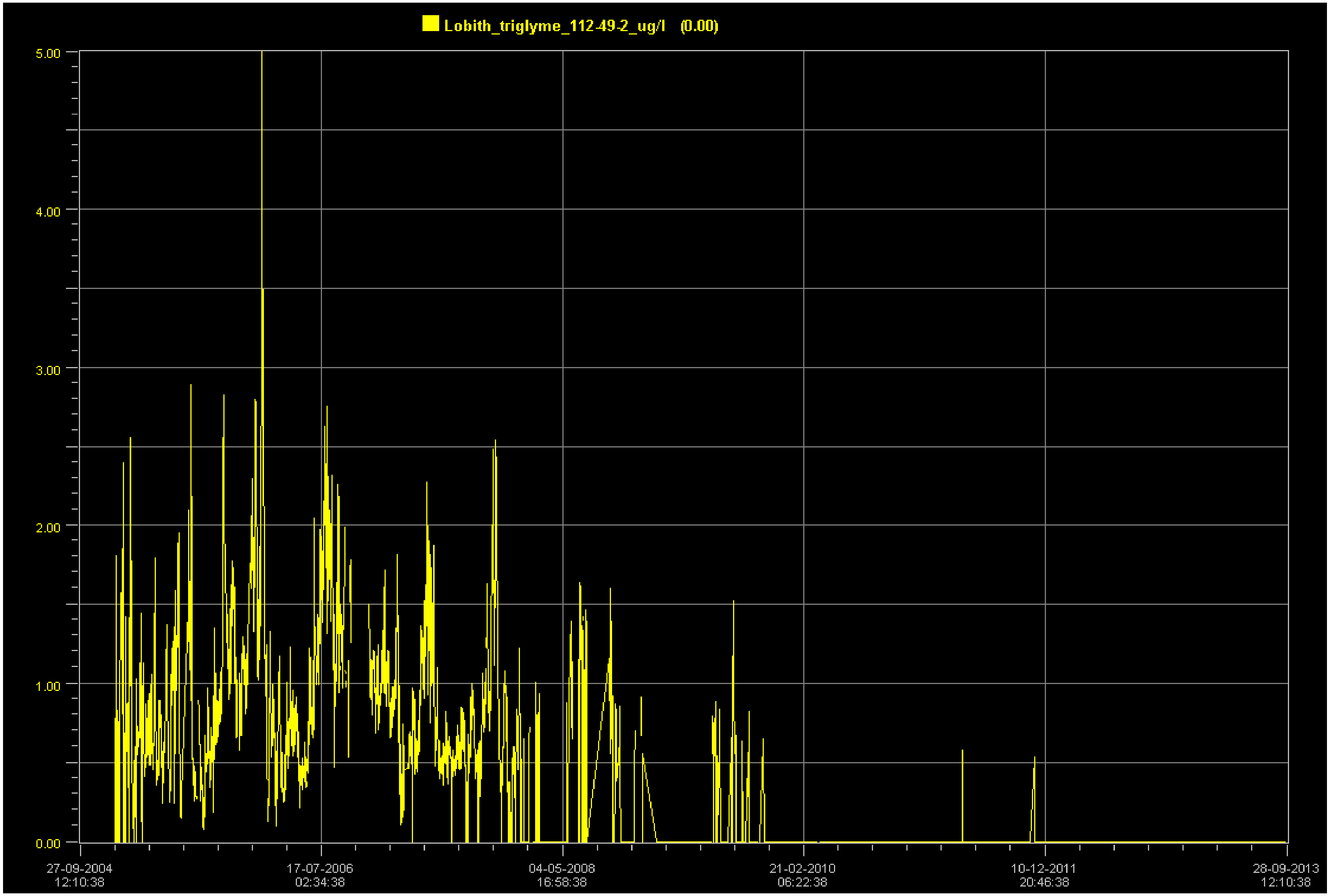
4.00
3.00
2.00
1.00
0.00
31-08-2004 00:00:00
25-06-2006 04:48:00
18-04-2008 09:36:00
10-02-2010 13:24:00
05-12-2011 18:12:00
29-09-2013 00:00:00

b)


Lobith_diglyme_111-96-6_ug/l (3.87)
10.00
8.00
6.00
4.00
2.00
0.00
31-08-2004 00:00:00
25-06-2006 04:48:00
18-04-2008 09:36:00
10-02-2010 13:24:00
05-12-2011 18:12:00
29-09-2013 00:00:00

c)



🟨 Lobith_triglyme_112-49-2_ug/l (0.00)
5.00
4.00
3.00
2.00
1.00
0.00
27-09-2004 12:10:38
17-07-2006 02:34:38
04-05-2008 16:58:38
21-02-2010 06:22:38
10-12-2011 20:46:38
28-09-2013 12:10:38

d)

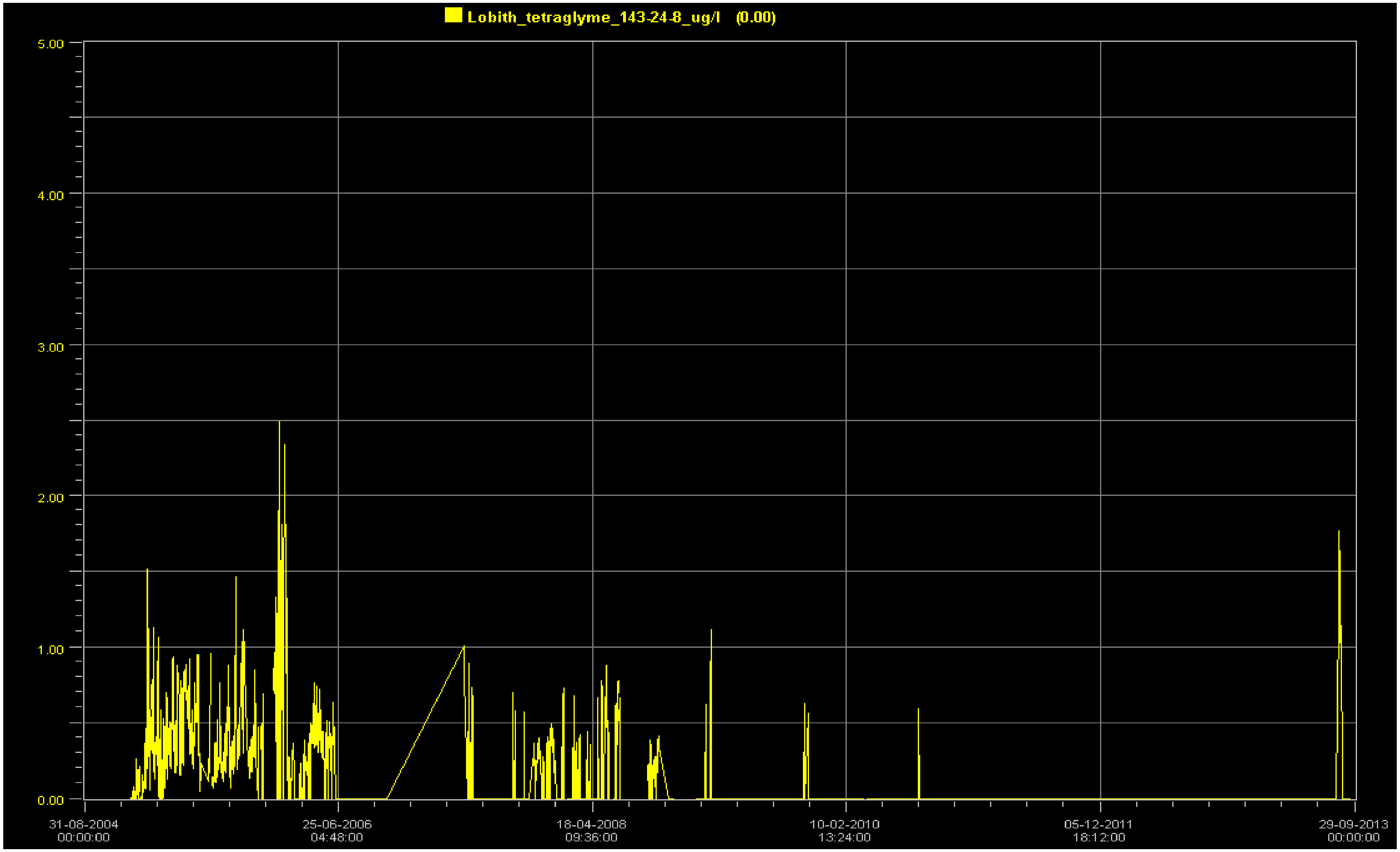


FIGURE A. 2 Historical concentrations of a) ETBE, b) diglyme, c) triglyme, and d) tetraglyme in the Rhine River at the measuring station Lobith (*Source*: IAWR, 2013)

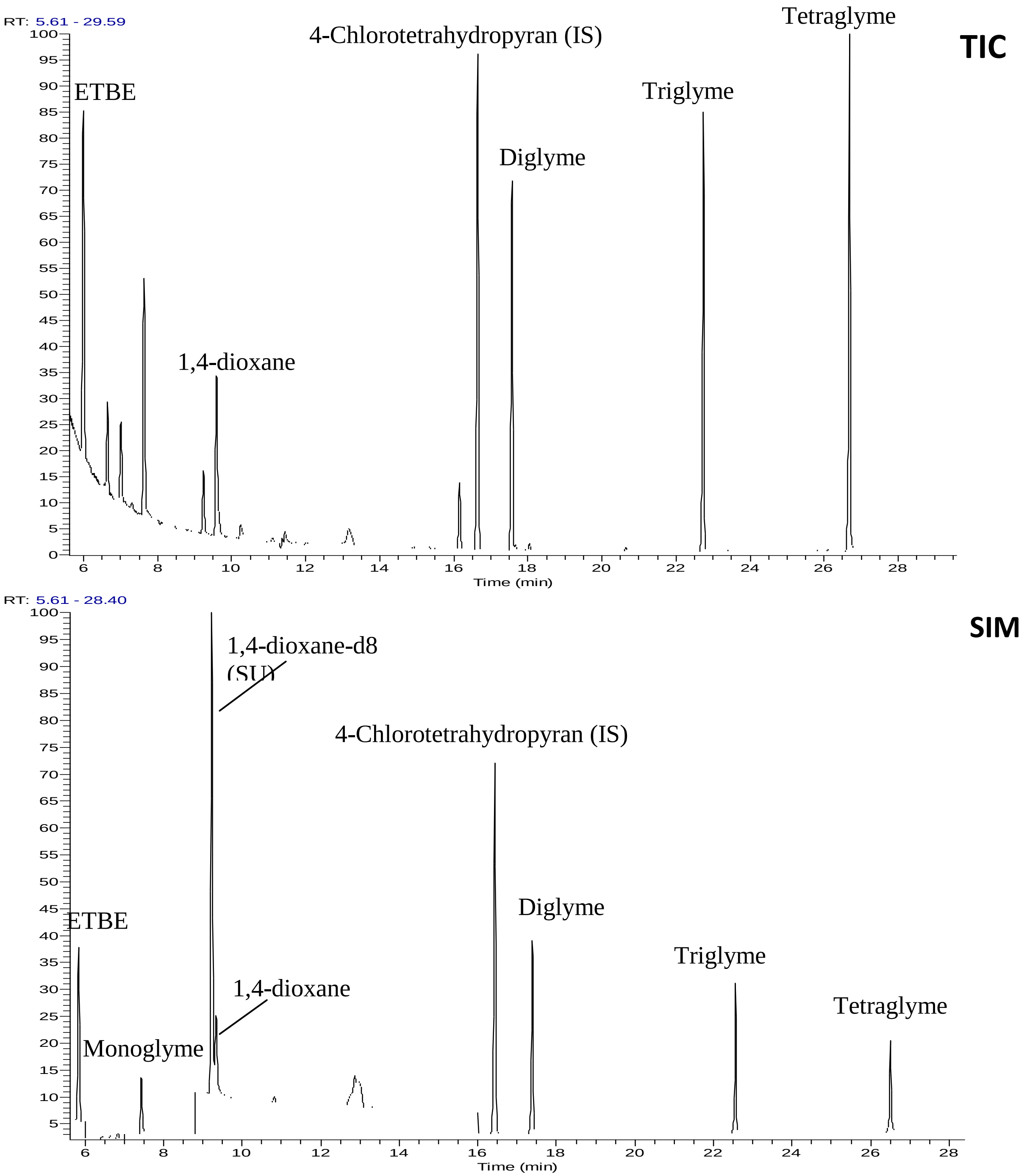


FIGURE A. 3 GC/MS chromatogram of the target analytes: ETBE, monoglyme 1,4-dioxane, 1,4-dioxane-d_8 (Surrogate), 4-chlorotetrahydropyran (Internal Standard), diglyme, triglyme and tetraglyme in total ion chromatogram (TIC) and selected ion monitoring (SIM).

Publications

- Stepien, D.K. & Püttmann, W. Simultaneous determination of six hydrophilic ethers at trace levels using coconut charcoal adsorbent and gas chromatography/mass spectrometry. Anal Bioanal Chem **2013**, 405, 1743-1751.
- Stepien, D.K., Regnery, J., Merz, C., Püttmann, W. Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany. Sci Total Environ **2013**, 458-460, 150-159.
- Stepien, D.K., Diehl, P., Helm, J., Thoms, A., Püttmann, W. Fate of 1,4-dioxane in the aquatic environment: from sewage to drinking water. Water Res **2014**, 48, 406-419.
- Stepien, D.K., Püttmann, W. Source identification of high glyme concentrations in the Oder River. Water Res **2014**, DOI: 10.1016/j.watres.2014.01.067.

Abstracts

- Stepien, D.K., Püttmann, W. Quantitative Determination of Hydrophilic Ether Species in Surface Waters by Solid Phase Extraction and Gas Chromatography/Mass Spectrometry (SPE GC/MS). The society of Environmental Toxicology and Chemistry (SETAC), 6th SETAC World Congress 2012 (May), Berlin, Germany. **Poster presentation.**
- Stepien, D.K., Regnery, J., Merz, C., Püttmann, W. Determination of organophosphates and hydrophilic ethers in groundwater of the Oderbruch polder (Germany) by solid-phase extraction (SPE) and gas chromatography / mass spectrometry (GC/MS). Groundwater Vulnerability – Emerging issues and new approaches (GW-IMVUL), Paris, France, July 2012. **Oral presentation.**
- Stepien, D.K., Püttmann,W. Simultaneous determination of hydrophilic ethers species in the surface waters by solid-phase extraction and gas chromatography/mass spectrometry. Thermo Scientific GC & GC-MS Anwenderseminar. Mainz, Germany, March 2013. **Oral presentation.**
- Stepien-Demers, D.K., Püttmann,W. Persistent hydrophilic ethers (1,4-dioxane and glymes) in surface- and groundwaters. 14th EuCheMS International Conference on Chemistry and the Environment (ICCE), Barcelona, Spain, June 2013. **Oral presentation.**

Curriculum Vitae

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Related courses: Environmental Resource, - Policy, -Mgmt, - Disasters
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