Organic Trace Substances Relevant for Drinking Water

Assessing their Elimination through Bank Filtration – Phase 1

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Abstract

The project "Organic Trace Substances Relevant for Drinking Water – Assessing their Elimination through Bank Filtration (TRACE)" aims at giving an up-to-date overview of the potential risk resulting from the occurrence of chelating agents, perfluorinated compounds (PFCs) and selected pesticides in surface waters and to show if there is a potential for the substances to persist during bank filtration and artificial recharge. During the first phase of the project which is subject of this paper, a literature study was conducted addressing their occurrence (in the Berlin region and elsewhere), amounts produced as well as data on their persistence in the subsurface. This was the basis for a decision on the substance applied in the field scale experiments at the UBAs experimental field during the following project phase. Using freely available databases (e.g. ULIDAT, DIMDI, Tiborder) 1148 references were screened for their relevance to these topics, and 450 of these were classified as relevant. Of these, so far the 223 most important references have been compiled in an ACCESS database which comprises data on the data origin as well as on specific values (e.g. measured concentrations, amounts produced, use, main metabolites, sources, pathways in the environment). The database links this information so that output forms ("fact sheets") can be created that summarize all data for one specific substance. The regarded substances were subsequently classified according to the criteria: usage / production, occurrence in surface water (if possible also in groundwater and bank filtrate), degradation potential, biological degradability, production of relevant metabolites and toxicity.

For the chelating agents three substance groups were examined closely: aminocarboxylates, hydrocarboxylates and phosphonates (all other substance groups were found to be irrelevant due to total biodegradability). The aminocarboxylates are produced in highest numbers and occur most frequently (especially EDTA, PDTA, NTA and DTPA). There are, however, already extensive investigations on this field so that few knowledge gaps were identified. Hydrocarboxylates are produced in lesser amounts and for some ready biological degradability has been shown. For these reasons further investigations were not seen as a priority. Phosphonates produce relevant metabolites (phosphates that enhance eutrophication) and are produced in high amounts (> 1000 t/a). This substance group was therefore recommended for further investigations.

Currently a variety of research projects cover the field of perfluorinated compounds (PFCs) that occur in aquatic environments world wide and whose toxicity and persistence is not yet clearly determined. Most investigations aim at the main substances of this group: PFOA and PFOS. These are, however, currently being replaced by shorter chained PFCs on which investigations are lacking. This substance group is therefore also of interest for further investigations.

For the pesticides glyphosate and isoproturone high production rates and frequent occurrence in surface and groundwater world wide were determined. Due to this fact and to the presence of relevant metabolites (e.g. AMPA) as well as to limited knowledge on their fate during underground passage these substances were classified as highly interesting for further investigations.

1. Introduction

Background

Organic complexing (or chelating) agents like EDTA (ethylendiamintetraacetic acid), NTA (nitrilotriacetic acid), PDTA (propylenediamintetraacetic acid) or DTPA (diethylentriaminpentaacetic acid) have a broad field of technical applications and are being used in great amounts. However, some are hardly removed by conventional methods of biological, chemical and physical waste water and drinking water treatment and can therefore be detected in the aquatic environment as well as in drinking water in ranges of some mg/L and a few µg/L, respectively.

For drinking water treatment plants using mainly bank filtered water, chelating agents might pose a threat for drinking water quality due to their chelating characteristics that, for example, might enhance heavy metal migration.

For these reasons EDTA became a substance widely monitored in water samples, as well as in many cases NTA and DTPA. For EDTA it is known that is has a very low degradation potential and it is hardly removed by underground passage and bank filtration. In 1991 the German industry committed themselves to reduce the discharge of EDTA into surface waters by 50 %. Though this aim has not been achieved yet, a substantial reduction of 30% to 40 % has been observed in surface waters in southern Germany (Baden-Württemberg).

However, other chelating agents (e.g. NTA, DTPA, IDS – iminodisuccinat and EDDS – ethylendiaminindisuccinat) are being used as substitutes and little is known about their elimination through underground passage.

Pesticides are also substances of concern for bank filtration sites, because they are known to occur in surface waters and they may potentially also resist degradation while migrating into the groundwater. Glyphosate and isoproturon (IPT, or abbreviated IPU in most English literature) are the most commonly used herbicides worldwide, not only in agriculture but also for railway treatment, as single compounds or in combination. Glyphosate is additionally applied in private gardens.

Perfluorinated compounds (PFCs) - in Germany usually called perfluorinated tensids (PFTs) - are found ubiquitously in aquatic environments. Currently, high concentrations in the river Möhne and Ruhr but also in drinking water from this region pointed out the need for more information about the substances themselves and their degradation potential. Though little is known about their retention in drinking water treatment systems, break-through in some supplies indicates that information about the performance of underground filtration regarding their retention is urgently needed.

Aim and scope of the TRACE project

The objectives of the study are to give an up-to-date overview of the potential risk resulting from the occurrence of the mentioned chelating agents, pesticides and PFCs in surface waters and to show if there is a potential for the substances to persist during bank filtration and artificial recharge.

The project will be structured as follows: 1) a literature review, 2) field observations in the Berlin region and 3) technical scale experiments at the UBA's experimental field.

Aim of the literature study

The first phase of the project TRACE (the literature study) had the aim to compile information on i) complexing agents (DTPA, NTA, PDTA, EDDS, IDS, and others), ii) perfluorinated compounds (PFCs) and iii) pesticides (e.g. isoproturon and glyphosate) with respect to their occurrence and significance for drinking water supplies using underground passage as (pre-) treatment method.

The literature study should address the following issues:

- Which are the complexing agents and PFCs most commonly used nationally and internationally?
- How high are the reported concentrations of these agents as well as those of the herbicides isoprotoron (IPT) and glyphosate in surface waters and do samples from the Berlin region (if values exist to date) fit into this frame?
- How do investigations conducted so far assess elimination through underground passage?
- Is there a possibility of these compounds breaking through into drinking water at bank filtration sites?

The resulting information was to be compiled and interpreted with respect to the question, which substance needs further investigation during the 2nd phase of the project, the field monitoring and the experiments at the UBA's experimental field.

2. Methods

In the beginning of the literature study information about the substances (i) chemical and physical parameters, and ii) other relating substances) mentioned above were searched in the internet using free available databases for references (e.g. ULIDAT, DIMDI, Tiborder). For most substances characteristic data were available in datasheets from the producers, few were also taken from journal articles.

The data of the substances and the references were compiled in an ACCESS database. Here different table sheets were used for references, substance data, elimination data, occurrences and other relevant data. The tables were cross-linked, to make it possible to create various queries while searching for substances or reference specific information.

If possible, elimination rates and half lives were classified as
- biological
- chemical
- photolytical
- hydrolytical
- catalytical
- adsorptive

with respect to results given by experiments in laboratory or technical scale or by field data. Similarly, surface water information was classified into
- sewage water
- surface water
- runoff
- lechate (SW)
- ground water (GW)
- well water (BW)
- raw water (RW)
- drinking water (TW)
- not defined (n.def., meaning no information on the water matrix was given in the literature, but it may refer to surface water)

Further information on production, use, main metabolites, source or pathway into the aquatic environment of the substances and groups were also included in the project database

Forms were created i) for input of the reference information and ii) to print out so-called fact-sheets of the substances.

The fact-sheets include substance names, chemical characteristics, physical characteristics, elimination potential, production data, ranges of concentrations in different water matrices, toxicity data as well as information to source and fate.

3. Results
The Project Database
At present the project database contains 1101 listed references from the years 1970 to 2007. Of these 880 (77 %) have been evaluated with respect to their significance for the project (table 1). 460 publications (40 %) were found to be relevant and the data of the 237 most relevant articles has been added to the data base so far.

Table 1: Working status of the literature study.

Status	Chelates	Pesticides	Metabolites (AMPA, NDMA)	PFCs	unknown*	Sum
Relevant and added to database	54	96	19	52	2	223
Relevant but not yet added to database	37	64	24	107	5	237
Not (yet) relevant, / incomplete data / secondary literature	180	76	42	82	40	420
Not yet evaluated	63	123	23	37	22	268
Sum	334	359	108	278	69	1148

*no substance or substance-group named

About 134 substances and 16 substance groups are currently listed in the project database. Of these 32 were chosen to be relevant for the literature study.

Table 2: Number of substances in the project database.

	Chelates	Pesticides	Metabolites (AMPA, NDMA)	PFCs	Sum
Number of groups	7	3	2	4	16
Number of substances	28	7	11	82	134
Number of relevant substances	19	4	2	7	32

Evaluation of the Relevance and Persistence of Complexing Agents (Chelates)
Complexing agents are mainly used in detergents, paper industry, textile industry, photo industry, metal industry, cosmetics, pharmaceuticals, cooling systems, etc.
They are divided into the following subgroups:
1. Aminocarboxylates
2. Hdrocarboxylates
3. Phosphonates
4. Phosphates
5. Gluconates
6. Tartrates
7. Citrates

The groups 4 to 7 are well degradable under almost all conditions, so they were not included in the literature study. This is also true for NTA (nitrilotriacetic acid) and DTPA (diethylenetriamine-pentaacetic acid) (both aminocarboxylates) for which extensive information about their behaviour during underground passage is available (e.g. Stumpf et al. 1996; Schmidt 2005; Schmidt & Lange 2006). For NTA total mineralization is achieved (e.g. Schmidt & Brauch 2003), however there are indications DTPA to degrade to NTA and EDTA (ethylendiamintetraacetic acid) (Schmidt & Lange 2006). Due to this fact, DTPA is also

handled as a problematic substance which should be substituted by other chelating agents as well as the poorer degradable PDTA (propylenediamintetraacetic acid) - the second major substitute for ETDA - which is already being replaced by the photo industry (using ADA - alanindiacetic acid - and IBP - iminosuccinicpropionic acid - presently).

The criteria for choosing a suitable substitutes are:

- It should be similar in use and behaviour to the previously used complexing agent
- It should be well degradable, without having toxic metabolites, or should be totally mineralized
- It should not enhance eutrophication.

Phosphonates are often used substitutes, but they are less degradable with increasing molecule size and they also contain phosphate which promotes eutrophication of surface waters.

The main sources for input into the aquatic environment are the industry and the sewage water plants. There concentrations observed range from few µg/L up to maximum loads of 20 mg/L. In surface water only concentrations for DTPA and NTA are available, since they are part of many monitoring programs. The quality standards for DTPA and NTA in surface water of 10 µg/L and 5 or 10 µg/L, respectively, are not achieved in many cases (Schmidt & Brauch 2003; UBA 2006a).

For chelates only degradation rates in percent were found (see figure 2). DTPMP (diethylenetriamine penta (methylene phosphonic acid)), EDTMP (ethylenediamine tetramethylene (sodium) phosphonic acid), HEDP (1-hydroxyethane-1,1-diphosphonic acid), PBTC (2- phosphonobutane-1,2,4-tricarboxylic acid) (all phosphonates) and PDTA (an aminocarboxylate) are worse or less degradable than ATMP (amino tri(methylene phosphonic acid)) (a phosphonate), ADA, DTPA and IDS (iminodisuccinic acid) (all aminocarboxylates). Best degradable are NTA and MGDA (methylene glycine diacetic acid) (both aminocarboxylates). EDDS (ethylene diamine N,N'-disuccinic acid) (an aminocarboxylate) is special, because the degradation rate depends on the kind of stereoisomer. Four stereoisomers are known and one (S,S-EDDS) is very good degradable, R,R-EDDS is more or less impossible to degrade and the other ones (R,S- and S,R-EDDS) are intermediately degradable (Schowanek et al. 1997).

Pesticides

Since the 1970s pesticides are found in groundwater, but until now little is known about their degradation or elimination during groundwater flow or bank filtration.

Possible sources for pesticides in surface water are (Sturm & Kiefer 2006):

Diffuse sources:
- event-based runoff
- transportation through soil via burrows, macropores, etc.
- tile drainages
- effluence of contaminated groundwater into surface water
- wind drift during application
- input of previously evaporated pesticides

Point sources (Wolf 2005; Bach 2005):
- farm run-off
- sewage treatment plants

A further problem is often the use of pesticides close to surface water (below the minimum distance, UBA 2006b).

Contamination of surface water is mainly due to surface runoff and effluent from smaller wastewater treatment plants with frequently high input rates from farmyards. Groundwater is primarily contaminated by release of herbicides from topsoil and further transport through the vadose zone to the aquifer (Fobbe et al. 2006).

Since no data for concentrations in ground- and bank filtered water are available, the concentrations are calculated (= PEC: predicted environmental concentration) using the model PELMO (groundwater) and EXPOSIT (bank filtration) (BVL 2004), but with lack information about the exact substance characteristics on sorption and degradation potential (Märker et al. 2000).

In Germany, the quality standard for pesticides and their degradation products in groundwater and the threshold for drinking water are both 0.1 µg/L (e.g. IKSR 2000; Böhm et al. 2002). Occurrences > 0.1 µg/L trigger further investigations (Sturm & Kiefer 2006).

Glyphosate

Glyphosate is the most commonly used herbicide worldwide. Because of its universal application, it is classified as a total herbicide. It is used in agriculture and for non-agricultural uses at railways and in private gardens (e.g. Bruno & Schaper 2002).

Glyphosate belongs to the phosphorous herbicides and was developed in the end of the 1950s. It has been in frequent use in agriculture since 1971. Since about 2000 it has been the most sold and most expanding herbicide worldwide.

Its main metabolite is AMPA, which has been included in the literature study because of its relevance for ground- and drinking water quality.

Concerning its occurrence (see figure 1A), there is no data for glyphosate in sewage water available, but in surface water average concentrations of 162 µg/L and maximum concentrations of 1,700 µg/L were detected. Runoff concentrations reach 1.84 µg/L and it was also found once in groundwater with a concentration of 0.54 µg/L (exceeding the target value for pesticides).

The degradation of glyphosate is intermediate (see figure 2 and 3), but it can also persist in the ground for more than one year showing its relevance for groundwater recharge.

Isoproturon

Isoproturon (IPT) is a phenylurea derivate and is mainly used in cereal agriculture. It is also frequently used on railway tracks in combination with glyphosate.

Occurrences of IPT (see figure 1A) in sewage water are only given with a maximum of about 13.5 µg/L, in surface water it occurs in concentrations between ND (not detected) and 2 µg/L with a maximum of 35.9 µg/L. In groundwater IPT concentrations reach values above the target value, however, in raw water only concentrations below the threshold for drinking water were found.

The degradation potential of IPT (see figure 2 and 3) is less than that of glyphosate so it has more potential to persist and cause a breakthrough in bank filtration.

Tolylfluanide (Euparen)

Tolylfluanide is in use as fungicide, insecticide and herbicide in fruit- and wine culturing. Tolylfluanide is presently a substance of concern (DVGW 20906), because it is transformed to the nitrosamine NDMA during ozonation in the drinking water treatment process. Since nitrosamines are highly toxic and cancerogenic (Preussmann 1983) the removal of tolylfluanide during underground passage should be achieved. There is, however, very little information on its degradation potential (65-81 % due to simulated and natural rainfalls, Benz et al.; see figure 2) and nothing on its occurrence in the environment.

Metabolites

AMPA

AMPA is the main degradation product of phosphonates (e.g. Klinger et al. 2000) used as chelating agents and pesticides like glyphosate (e.g. Cox 2000). AMPA is part of many monitoring programs of surface waters together with the pesticide glyphosate. Normal

concentrations range from the detection limit to 6 µg/L and a maximum of about 35 µg/L has been reported. A monitoring of runoff water in Bavaria reported by Henkelmann (2001) shows a mean value of only 0.33 µg/L which might be due to the good degadation potential of AMPA. It's relevance for surface waters is mainly due to the fact that it is degraded to phosphate, thus enhancing eutrophication of surface waters.

Nitrosamines
Since the 1960s it is known that nitrosamines are carcinogenic. Since then the input source of nitrosamines and their precursors were investigated in numerous research projects (Preussmann 1983). Currently, nitrosamines are new in the focus of drinking water treatment (DVGW 2006) since they are metabolites that occur during ozonation or chlorination (e.g. Chang et al. 2000) of the pesticide tolylfluanide.
NDMA
Precursors of NDMA are pharmaceuticals (e.g. Eisenbrand 1983), products from the rubber industry (Spiegelhalder 1983) and pesticides. Therefore NDMA is found in sewage, surface and groundwater with decreasing concentrations due to its good degradability potential. However, it is also a metabolite that occurs during drinking water treatment and therefore higher concentrations can be found in drinking water than in the groundwater with values (0.15 µg/L) above the threshold for drinking water (if classified as a pesticide metabolite). In the US (California) and Canada (Ontario) different standards or quality standards for drinking water are in use with values of about 0.003 to 0.2 µg/L (e.g. Choi & Valentine 2003; DHS 2006).

Perfluorinated Compounds (PFCs)
PFCs have been produced since the 1950s. The main producers are 3M and DuPont. So far about 850 perfluorinated substances are known (Schulte 2007).
Due to their hydrophobic, lipophobic and dirt repelling characteristics they have a wide range of use in textile industry, coatings, surface refinement, fire extinguishers and as solvent intermediates.
Caused by their various and extensive use PFCs occur worldwide in the aquatic environment, also in the oceans and in all kind of biota.
PFCs are divided into 4 subgroups and each subgroup contains various substances or again subgroups.
- Perfluorocarbons (PFC)
  volatile substances which enforce the greenhouse effect
- Fluorotelomer alcohols (FTOH)
- Perfluorosulfonates (PFAS)
  most common related substance is PFOS
- Perfluorocarboxylic acid (PFCA)
most common related substance is PFOA, which is mainly used for FTOH production
Further on, the PFCs are classified by their C-chain length in shorter chained (≤8 carbons) and longer chained (≥9 carbons) compounds.
The main source for the input of PFCs is the industry as well as sewage sludge (e.g. added to soils as fertilizers), fire fighting foams and others.
Since the year 2000 extensive research has been carried out on the occurrence and degradation of PFCs. Therefore it is known, that PFCs meet the characteristic of POPs (Polar Organic Pollutants) and PFOS additionally those of PBTs (Persistent Bioaccumulating Toxins) because of its toxicity.
PFOS is also the main natural metabolite of the most commonly used PFCs, which is why increasing concentrations can be found during sewage water treatment. Under extreme conditions like in an advanced sewage water treatment plant shorter chained PFCs and free

fluoride can be detected. Under natural conditions the C-F bond of the carbon moiety is stable, which is the reason for their persistence in the environment and only the active moiety (e.g. carboxylic group) can be metabolized.

In 2006 fluoropolymer producers agreed to follow the PFOA Stewardship programme (US EPA, 25.01.2006) which envisages to reduce the emission of PFOA in all environmental media and the concentrations in other products by 95 % until 2010 (Ambrose & Clement 2006; TEGEWA 2006; EPA 2006). The two goals of the program are:

1) To achieve a 95 % reduction no later than 2010, measured from a year 2000 baseline, in facility emissions of PFOA (the 8 carbon PFCA), longer chain PFCAs and their precursor chemicals, as well as residuals in commercial products

2) To work toward the elimination of PFOA, longer chain PFCAs and their precursors from facility emissions and from residuals in commercial products by 2015

The Canadian Government reacted to the high amounts of PFCs with the Canadian Environmental Protection Act (Department of the Environment Canada 1999), which requires that no new substances should be introduced into Canadian commerce without first being assessed to determine if it could pose a risk to human health or the environment, and with the Canada Action plan under CEPA (Environment Canada 2006).

In Europe the European parliament agreed on the text of a guide line restricting PFOS on Oct. 25th 2006. Actions shall be carried out following to a risk assessment.

In this literature study the 4 main subgroups of the PFCs (i.e. PFC, FTOH, PFAS, PFCA) as well as PFOA and PFOS as the main representatives were investigated. The range of concentrations depends on the distance to an input source. In surface water usually only a few µg/L can be observed. However, closer to a point source (sewage treatment plant etc.) values can increase up to maximum concentrations of mg/L. Similar observations were made in groundwater possibly be influenced by sewage sludge application to crop land.

4. Summary and Conclusions

For the 2nd phase of the project (field observations and experiments) it was necessary to chose two substances from the 32 substances of the literature study using the following criteria:

- usage / production
- occurrence in surface water and possibly also in groundwater of bank filtrate
- degradation potential
- biological degradability
- production of relevant metabolites
- toxicity (LD$_{50}$ oral rat)

Also of matter is how the substance will be used in future. For the complexing agents an agreement of the industry exists to reduce the emissions and to replace chelates of concern (e.g. EDTA, DTPA) by substitutes. Pesticides and their metabolites are strongly ruled in use and dosage, so that concentrations in ground- and drinking water should not exceed 0.1 µg/L. And in the Stewardship program the PFCs producing industry commits themselves to reduce the emission or to substitute these substances by better degradable substitutes

All criteria were given the same weight.

Table 3: Summary of criteria for the relevant substances (empty boxes: no information).

	Production[1]	Occurrence (surface water) [2]	Occurrence (groundwater / bank filtrate)[3]	Biological degradablity[4]	Relevant metabolites[5]	LD$_{50}$ oral rat [6]
Chelating Agents						
Aminocarboxylates						
ADA	-	+		+	?	- / +
DTPA	-	++	+	-	+	- / +
EDDS	+			(-)	+	
IBP						
IDS	+			+		
MGDA	+			++		
MIDA						
NTA	++	+	+	++	+	+
PDTA	++			-	+	+
Hydroxocarboxylates						
DHEG	-			+		
HEDTA	-			+		
HEIDA	-					
THPED	-			+		
Phosphonates						
ATMP/NTMP	++	+		-	++	
DTPMP	++	+		-	++	
EDTMP	++	+		-	++	
HDTMP	-			-	++	
HEDP	++			-	++	+
PBTC	++	+		-		
Pesticides						
Glyphosate	++	++	++	+	++	- / +
Isoproturon (IPT/IPU)	++	++	++	+	++	+
Tolylfluanide				+	++	-
Metabolites						
AMPA		++		-	++	-
NDMA		++	++	+	+	++
PFCs						
PFC	+			-		
FTOH				- / +	++	
PFAS	+	+		-		
PFOS	-	+	++	-		++ / +
PFCA		+		-		

	Production[1]	Occurrence (surface water) [2]	Occurrence (groundwater / bank filtrate) [3]	Biological degradablity [4]	Relevant metabolites [5]	LD$_{50}$ oral rat [6]
PFOA	+	++	++	- / +	++	

1) -: <100 t/a; +: 100-1000 t/a; ++: >1000 t/a
2) +: positives in surface or waste water; ++: >10 µg/L
3) +: positives (e.g. in raw water); ++: >0.1 µg/L
4) -: not/badly biodegradable; +: not readily biodegradable; ++: easily biodegradable
5) ?: not identified yet; +: metabolites identified; ++: relevant metabolites (e.g. phosphate, PFOA)
6) -: >5000 mg/kg bw; +: 100-5000 mg/kg bw; ++: <100 mg/kg bw

1. Chelating Agents
    - Aminocarboxylates are well investigated concerning their occurrences and fate during bank filtration. Although there are still high concentrations in surface and drinking water of EDTA, DTPA, NTA and PDTA, it is seen as a political and management problem, which is not the scope of this research project.
    - Hydrocarboxylates are produced only in small amounts and therefore not seen as relevant for drinking water resources in general.
    - Phosphonates are produced in high numbers and also meet the other above mentioned criteria, but since they have a high adsorption capacity, a threat to drinking water is not expected.
2. Pesticides
    - Glyphosate and IPT are produced at high rates and are found in surface and groundwater of different countries as well as in the river Havel (LUA Brandenburg, 2006). Both have relevant metabolites and their mobility in the subsurface as well as their persistence may lead to breakthrough during bank filtration. So far there have been little investigations on this field. Therefore both substances were chosen for the 2nd phase of the project: The technical scale experiments at the UBA's experimental field site will be carried out with glyphosate. The surface- and groundwater monitoring will cover glyphosate and IPT.
    - For tolylfluanide there is only little information on production and degradation. However, relevant metabolites (NDMA) are produced during ozonation. On the other hand tolylfluanide is not relevant for the Berlin region, regarding the drinking water treatment process and its usage.
3. Metabolites
    - The metabolite AMPA will be part of the 2nd phase as its precursor glyphosate is involved.
4. PFCs
    - PFOA and PFOS are the main substances of interest in this group. Extensive research is currently being carried out. No further investigations on PFCs will be carried out within this project.

5. Outlook
The literature study (complete input of literature data) will be continued until the end of the project for the relevant substances. This will also include the calculation of degradation rates

and half lives, if possible, and the implementation of working forms in the project-database for further use.

References
Ambrose, R., T. Clement (2006) Government Notes: Department of the Environment, Department of Health - Notice of Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors. Canada Gazette 140(24), http://canadagazette.gc.ca.

Bach, M. (2005) Pflanzenschutzmittel-Einträge über Kläranlagen. Pflanzenschutzmittel und Gewässer, Bayrisches Landesamt für Wasserwirtschaft, 191-203.

Benz, S., M. Schmitz-Eiberger, G. Noga. Regenfestigkeit von Kontaktfungiziden und ihre Einflussfaktoren. Institut für Obstbau und Gemüsebau Bonn.

Böhm, E., T. Hillenbrand, F. Marscheider-Weidemann (2002) Ermittlung der Quellen für die prioritären Stoffe nach Artikel 16 der Wasserrahmenrichtlinie und Abschätzung ihrer Eintragsmengen in die Gewässer in Deutschland. UBA-Texte 68/02.

Bruno, H., S. Schaper (2002) EU-Beurteilungsbericht Glyphosat - Rechtliche Regelungen der Europäischen Union zu Pflanzenschutzmitteln und deren Wirkstoffen. Berichte aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft, Biologische Bundesanstalt für Land- und Forstwirtschaft, Braunschweig, Deutschland, Abteilung für Pflanzenschutzmittel und Anwendungstechnik, D26 (94).

BVL (2004) Technische Hinweise zum Zulassungsverfahren: Naturhaushalt. Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, www.bvl.bund.de.

BVL (2005) EU-Wirkstoffprüfung. Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, www.bvl.bund.de.

Chang, C.-Y., Y.-H. Hsieh, S.-S. Hsu (2000) The formation of disinfection by-products in water treated with chlorine dioxide. Journal of Hazardous Materials : Management, Handling, Disposal, Risk Assessment, B79: 89-102.

Choi, J., R.L. Valentine (2003) N-nitrosodimethylamine formation by free-chlorine-enhaced nitrosation of dimethylamine. Environmental science & technology, 37(21): 4871-4876.

Cox, C. (2000) Glyphosate Factsheet. http://www.mindfully.org/Pesticide/Roundup-Glyphosate-Factsheet-Cox.htm.

Department of the Environment Canada (1999) Priority substances list assessment report: Canadian environmental protection act. [Ottawa]: Minister of Public Works and Government Services, ISBN 0-662-29137-9, VI: 64 p.

DHS (2006) California Drinking Water: Activities Related to NDMA and other Nitrosamines. www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/NDMAindex.htm.

DVGW (2006) Einsatz von Pflanzenschutzmitteln und Bildung des Nitrosamins NDMA im Rahmen der Rohwasseraufbereitung. DVGW-Rundschreiben W 04/06 vom 24.11.2006 an die Geschäftsleitung der DVGW-Gas/Wasser- und DVGW-Wasserversorgungsunternehmen.

Eisenbrand, G. (1983): Nitrosierung von Arzneimitteln. In: R. Preussmann (Ed.) Das Nitrosamin-Problem, Rundgespräche und Kolloquien/Deutsche Forschungsgemeinschaft, ISBN 3-527-27403-0, 213-221.

Environment Canada (2006) Risk Management Strategy For New Fluorotelomer Based Substances Prohibited Under Section 84 of CEPA 1999. www.ec.gc.ca.

EPA (2006) 2010/15 PFOA Stewardship Program. http://www.epa.gov/opptintr/pfoa/pubs/pfoastewardship.htm.

Fobbe, R., B. Kuhlmann, J. Nolte, G. Preuß, C. Skark, N. Zullei-Seibert (2006) Polar Herbicides and Metabolites. T. Reemtsma and M. Jekel (Eds.) Organic Pollutants in the

Water Cycle - Properties, Occurrence, Analysis and Environmental Relevance of Polar Compounds, Wiley-VCH Verlag GmbH & Co. KGaA Weinheim, 121-153.

Henkelmann, G. (2001) Untersuchungen von Wirkstofffrachten im Agrarökosystem - Monitoring und räumlich Modellierung des Wasserhaushalts, der Bestandesdynamik und der Stoffausträge in Oberflächengewässer und Grundwasser. Jahresbericht 2000 d. Forschungsverbunds Agrarökosysteme München (FAM). ISSN 0941-9063.

IKSR (2000) Zielvorgaben. Internationale Kommission zum Schutz des Rheins, Stand Juli 2000.

Klinger, J., F. Sacher, H.-J. Brauch (2000) Bildung von Glyphosat und AMPA bei der Ozonung: Ein Problem für die Wasserwerke? Vom Wasser 94: 149-159.

Märker, B., T. Urhahn, K. Ballschmiter (2000): Regionale Verteilungsmodelle für Chemikalien in Vergleich. Akademie für Technikfolgenabschätzung in Baden-Württemberg, Pilotstudie, ISBN 3-934629-18-0.

Preussmann, R. (1983) Das Nitrosamin-Problem. Bericht über das Abschlusskolloquium der Senatskommission zur Prüfung von Lebensmittelzusatz- und -inhaltsstoffen zum Schwerpunktprogramm "Analytik und Entstehung von N-Nitroso-Verbindungen" am 8. und 9. Oktober 1982 in Bonn / DFG, Dt. Forschungsgemeinsch, Rundgespräche und Kolloquien / Deutsche Forschungsgemeinschaft, XI, ISBN 3-527-27403-0.

Schmidt, C.K., H.-J. Brauch (2003) Aminopolycarbonsäuren in der aquatischen Umwelt: Quellen, Vorkommen, Umweltverhalten, Toxizität und Beseitigung. TZW- Schriftenreihe 20: 252 p.

Schmidt, C.K., T. Lange (2006) Exportorientierte Forschung und Entwicklung auf dem Gebiet der Wasserver- und -entsorgung Teil I: Trinkwasser; Schlussbericht Teilprojekt B6: Ermittlung der potenziellen Reinigungsleistung der Uferfiltration/Untergrundpassage hinsichtlich der Eliminierung. Abschlußbericht 02WT0280, ISBN 3-00-015478-7, 200 p.

Schowanek, D., T.C.J. Feijtel, C.M. Perkins, F.A. Hartman, T.W. Federle, R.J. Larson (1997) Biodegradation of (S,S), (R,R) and Mixed Stereoisomers of Ethylene Diamine Disuccinic Acid (EDDS), a Transition Metal Chelator. Chemosphere 34(11): 2375-2391.

Schulte, C. (2007) In-Thema: Perfluorierte Verbindungen. UWSF - Umweltwissenschaften und Schadstoff-Forschung - Zeitschrift für Umweltchemie und Ökotoxikologie 18(3): 149-150.

Spiegelhalder, B. (1983) Nitrosamine und Gummi. In: R. Preussmann (Ed.) Das Nitrosamin-Problem, Rundgespräche und Kolloquien/Deutsche Forschungsgemeinschaft, ISBN 3-527-27403-0, 235-244.

Sturm, S., J. Kiefer (2006) Pflanzenschutzmittel in Grund- und Oberflächenwässern Deutschlands - Befunde und Eintragspfade. In: Schriftenreihe Veröffentlichungen aus dem Technologiezentrum Wasser Karlsruhe, 30: Organische Spurenstoffe in der Wasserversorgung, 59-80.

Sturm, S., J. Kiefer, E. Eichhorn (2006) Befunde von Pflanzenschutzmitteln in Grund- und Oberflächenwässern und deren Eintragspfade. Bedeutung für die Wasserwirtschaft und das Zulassungsverfahren. Abschlussbericht zum DVGW-Forschungsvorhaben W 1/02/05, (in prep.).

TEGEWA (2006) Hintergrund zur Presseinformation „Wasserabweisende Textileschichtung von PFOS-Verbot nicht betroffen": Perfluorierte Verbindungen. Verband TEGEWA e.V.

UBA (2006a) Organische Umweltchemikalien. www.umweltbundesamt.de/wasser/themen/ow_s4_5.htm.

UBA (2006b) Anwendung von Pflanzenschutzmitteln in der Landwirtschaft - Ergebnisse von Untersuchungen des Umweltbundesamtes und Vergleich mit Erkenntnissen der Länder.

Waldmann, R. (2006) Vorstellung des Verfahrens der Fundaufklärung am Beispiel Bentazon. Gespräch bei der Deutschen Vereinigung des Gas- und Wasserfaches e.V. in Bonn am 07. Februar 2006 (Präsentation).

Wolf, B. (2005) Belastung der Oberflächengewässer in Deutschland mit PSM. Pflanzenschutzmittel und Gewässer, Bayrisches Landesamt für Wasserwirtschaft, 205-216.