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Properties of Atrazine and Bentazone

Project acronym: Aquisafe 2

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Preparation of this report was financed in part through funds provided by

VEOLIA
WATER

Berlin, Germany
2010

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Deliverable number

Aquisafe 2 D 5.1

Abstract

The project Aquisafe assesses the potential of selected near-natural mitigation systems, such as constructed wetlands or infiltration zones, to reduce diffuse pollution from agricultural sources and consequently protect surface water resources. A particular aim is the attenuation of nutrients and pesticides. Based on the review of available information and preliminary tests within Aquisafe 1 (2007-2009), the second project phase Aquisafe 2 (2009-2012) is structured along the following main components:

(i) Development and evaluation of GIS-based methods for the identification of diffuse pollution hotspots, as well as model-based tools for the simulation of nutrient reduction from mitigation zones

(ii) Assessment of nutrient retention capacity of different types of mitigation zones in international case studies in the Ic watershed in France and the Upper White River watershed in the USA under natural conditions, such as variable flow.

(iii) Identification of efficient mitigation zone designs for the retention of relevant pesticides in laboratory and technical scale experiments at UBA in Berlin.

The present report provides a review of the properties and existing mitigation experience of the two herbicides Atrazine and Bentazone, which will be examined exemplarily in (iii). Whereas Atrazine is clearly the pesticide of greatest concern in the USA, Bentazone is mainly an issue in Europe with an increasing tendency.

The sorption of Atrazine and Bentazone on soils is moderate. Moderate sorption in combination with medium to high persistency makes these compounds relatively mobile; therefore they can usually be observed in surface waters in general and in ground waters near places of their application. First experiences show that mitigation systems can be effective measures to decrease their concentrations by supporting biotic and abiotic dissipation processes, mainly at high residence times.

Adding organic matter can improve adsorption of Atrazine and Bentazone, an important dissipation process in these systems. Degradation rates for Atrazine and for Bentazone can be increased by implementing highly microbiologically active conditions which can usually be accomplished in the presence of external carbon sources. While mineralization of both herbicides is favoured in aerobic -environments significant degradation of Atrazine was also observed under anaerobic conditions.

A great number of open questions remain on how to design a mitigation system which is adequate to reduce herbicides in drainage water. For instance, there is no specific information on the degradation of diluted and adsorbed forms of the herbicides, very little information about necessary residence times, adsorption constants, half lives and leaching behaviour in specific substrates or comparable designs. Moreover, the influence of nitrogen, which is present in drainage water at high concentrations, on degradation of Atrazine and Bentazone remains uncertain. Finally, the behaviour of Atrazine and Bentazone (contained in agricultural drainage water) in mitigation systems in general and in bioretention swales in particular is poorly studied.

Realistically, mitigation systems would only be implemented if they also allow significant reduction of nitrates. Given the existing knowledge, systems with both aerobic and anoxic zones are likely to bring most successful results regarding both herbicides and nitrates; though they may be difficult to implement. Both for nitrates and pesticides, the

presence of external organic carbon sources (with a combination of fast accessible and sustainable substrate partitions) seems to be a good basis for dissipation processes and effective reduction.

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Glossary

BfR: Bundesanstalt für Risikobewertung – Federal agency for risk evaluation (Germany)

CAS: Chemical Abstracts Service

DT_{50}: Disappearance half life refers to the time, in which half of a substance is transformed into its metabolites.

EC_{50}: The half maximum effective concentration refers to the concentration of a substance, which induces a definite response in 50 % of the test animal population.

GC/MS: Gas-chromatography with mass-spectrometry

GUS: The GUS leaching index assesses the leachability of molecules and the possibility of finding these compounds in groundwater. This index is based on two parameters: mobility in soil, given by the organic carbon partition coefficient K_{OC}, and soil persistence, quantified by the disappearance half-life in the soil DT_{50}, defined in field conditions and expressed in days.

HPLC/UV: High performance liquid chromatography with photometric detection (ultra violet frequency)

IFEN: Institut français de l'environnement – French Environmental Institute (France)

K_{Henry}: Henry – partition coefficient, which describes the ratio of concentration of a substance between gaseous phase (air) and liquid phase (water).

K_{OC}: Organic carbon partition coefficient, which describes the ratio of concentration of a substance between adsorbed and dissolved partition, independent of the organic content of the soil.

LC_{50}: The lethal concentration of a substance (mg/l), which induces death to 50 % of the test animal population.

LD_{50}: The lethal dose of a substance (mg/kg), which induces death to 50 % of the test animal population.

Log K_{OW}: Logarithm of the partition coefficient, which describes the ratio of concentrations of an un-ionized compound between two solutions, in this case octanol and water.

UBA: UmweltBundesAmt – Federal Environment Agency (Germany)

WHO: World Health Organisation

Chapter 1

Introduction

The project Aquisafe assesses the potential of selected near-natural mitigation systems, such as constructed wetlands or infiltration zones, to reduce diffuse pollution from agricultural sources and consequently protect surface water resources. A particular aim is the attenuation of nutrients and pesticides. Based on the review of available information and preliminary tests within Aquisafe 1 (2007-2009), the second project phase Aquisafe 2 (2009-2012) is structured along the following main components:

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(iii) Identification of efficient mitigation zone designs for the retention of relevant pesticides in laboratory and technical scale experiments at UBA in Berlin.

The present report provides a review of the properties of the two herbicides Atrazine and Bentazone, which will be examined exemplarily in (iii). Atrazine and Bentazone were selected based on specific substance characteristics, such as chemical and physical properties, analytical methods, trends of use and trends of concentrations in surface waters, treatability in drinking water plants, toxicity, regulatory thresholds and the importance of their metabolites and therefore their relevance for drinking water production (Aquisafe Technical Committee Meeting on 25th of June 2009 in Rennes). Whereas Atrazine is clearly the pesticide of greatest concern in the USA, Bentazone is mainly an issue in Europe with an increasing tendency.

The following report provides the most important properties of the two selected herbicides (chapters 2.1 and 2.2), highlights existing experiences in mitigation systems (chapter 3), draws conclusions on implications for the Aquisafe 2 project (chapter 4) and summarizes the findings in comparative tables (appendix).

Note that throughout the report, main sources are cited at the end of the respective paragraph, after the full stop. Other sources are indicated directly following the information, before the full stop.

Chapter 2

Fact sheets for the selected herbicides

2.1 Atrazine

Atrazine is on the market since 1957 (PPDB 2009). It is a systemic herbicide. Its phytotoxic action is defined by the inhibition of photosynthesis in the contaminated plant. Atrazine is used for control of broadleaf and grassy weeds, before and after plant emergence. It is applied on a number of crops, such as corn (= maize), sorghum, sugarcane, as well as for sweet corn, pineapple, Christmas trees and conifer reforestation plantings and lawns and golf courses. It is also used as a non-selective herbicide on non-cropped industrial lands and forests (EXOTOXNET 2009, US EPA 2003). Typical application times in temperate climate are shown in Tab. 1 for three most important crops.

Atrazine is mainly absorbed by the plants via their roots and also via their leaves and is distributed in the plant via the xylem (Schmidt in Litz et al. (Ed.) 2003).

Tab. 1: Typical application times for selected crops

Crop	**Application time**	
	pre-emergence	**post-emergence**
corn (= maize)	mid April to mid May	end of June
sorghum	mid June to mid July	end of August
sugar cane	in fall (directly at planting)	in the following spring at emergence and at canopy closure

2.1.1 Chemical and physical parameters

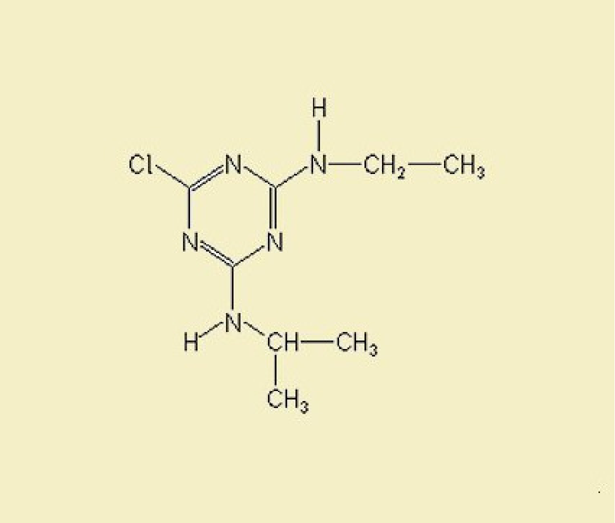

Fig. 1: Molecular structure Atrazine (PPDB 2009)

Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) has a medium solubility in water (33 mg/L at 22°C and pH 7, (28 mg/L at 28°C EXOTOXNET 2009)) and volatilizes barely (K_{HENRY}: 2,99 x10^{-4} Pa m³/mol (25°C)). Still, a drift of the substance to non-target areas via aerosols due to application methods, like spraying has to be anticipated. Atrazine dissociates (reversible change from non-polar molecule form into polar ion form) in water at low pH-values (pKa: 1.68 (22°C)). The distribution coefficient between Octanol and water (logKow) is 2.5 (moderate, 25°C) for Atrazine in its non-polar form (Schmidt in Litz et al. (Ed.) 2003).

The sorption on soil is medium (K_{oc}: 39-155 mL/g (Schmidt in Litz et al. (Ed.) 2003), 100 mL/g, EXOTOXNET 2009) and determined by clay minerals and organic material (Spongberg and Ganliang 1999). The risk for an enrichment of Atrazine and its metabolites in the soil (bound residues) is low (Schmidt in Litz et al. (Ed.) 2003).

Chemical hydrolysis (dechlorination) and degradation by soil microorganisms (dealkylation) account for most of the breakdown of Atrazine. In acidic or basic environments hydrolysis is rapid and the most important transformation pathway. At neutral pH values hydrolysis slows down and microbiologic degradation becomes dominant. Addition of organic material increases the rate of hydrolysis. In soils, Atrazine is characterised by a medium persistence against microbiological transformation in the aerobic soil (DT50: 35-50d, (146d, Gilliom et al. 2006)) and a high persistence in the deeper soil layers with low oxygen content (DT50: 105-200d). Favourable conditions for fast degradation are aerobic conditions and the efficiency of present microorganisms in catabolic (degradative) processes (not their amount or high temperatures). (Schmidt in Litz et al. (Ed.) 2003)

However, works by Ghosh & Philip (2003) indicate that the addition of carbon sources can enhance the degradation of Atrazine under denitrifying or even anaerobic conditions. Atrazine is moderately to highly mobile in soils with low clay or organic matter content. Because it does not adsorb strongly to soil particles and has a long half-life, it has a high potential for groundwater contamination (EXOTOXNET 2009). According to the GUS leaching potential index Atrazine is highly leachable (3.75, PPDB 2009; 3.6, Gan 2002).

Migration into deeper soil is also supported by macropores, which promote preferential flow and therefore shorter contact times and by adsorption of Atrazine to soil colloids and particles, which can be transported by water flow (Schmidt in Litz et al. (Ed.) 2003).

2.1.2 Analytical methods

Atrazine can easily be removed from water by solid phase extraction (Bohuss et al. 2005). It does not need to be derivatized and can be analysed by GC/MS. In the US EPA method 525.2 (Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry -Revision 2.0) a standard procedure, is published to allow international reproduction of the analytics. From soil, Atrazine has to be extracted by methanol (Del Valle et al. 1994). The main metabolites of Atrazine can probably be detected together with the parent compound, judged from their chemical structure.

Alternatively it would be possible to quantify all mentioned compounds due to their structure by HPLC/UV instead of GC/MS, however detection limits are higher and selectivity is lower. In France (CAE) Atrazine and DEA are analysed by HPLC/MS/MS with the same multiresidues method (pers. comm. P. Roche 2010), but a more selective detection method compared to HPLC/UV.

2.1.3 Trends of use/ trends in concentration in surface waters and groundwater

Use

Over a long period Atrazine was the most used conventional pesticide in agricultural use in the USA (1987 (71-76 million lbs.), 1993 (70-75 million lbs.), 1995 (68-73 million lbs.), 1997 (75-82 million lbs.), 1999 and 2001 (74-80 million lbs.)). Despite stable or slightly increased use, Atrazine was displaced from top position by Glyphosate (85-90 million lbs.) in 2001. (Kiely 2004)

Based on a survey between 1990 and 1997, 64 – 76 million pounds were used annually in the USA. 83%, 10% and 3% of this total US Atrazine use is applied to corn, sorghum and sugar cane, respectively. Less than 2% are used in forestry and non-agricultural proposes. In terms of cropped area, 75 % of all corn-fields, 56 % of all sorghum-fields, 76 % of all sugarcane-fields and 49-58 % of all sweet corn-fields are treated with Atrazine. (US EPA 2003)

The application rate of Atrazine varies remarkably between 0.4 and 4.5 kg/ha/yr in dependence on type of use (Burgoa B. & Wauchope R.D. 1995).

The use of Atrazine is restricted in Europe. Since 2004 Atrazine is on the EU list of banned herbicides; only Spain, Portugal, Ireland and the U.K. were allowed to use it under restrictions until 2007 (91/414/EWG). In some European states without EU membership, Atrazine is still a commonly used herbicide (PPDB 2009).

Surface water

Gilliom et al. (2006) found Atrazine during a U.S. stream survey between 1992-2001 in 90.2 % of all examined surface waters (rank 1 of the most frequently detected conventional pesticides) and in 42.9 % with concentrations above 0.1 µg/L (rank 1). In a more recent study (2004-2005) in the USA Kingsbury et al. (2008) found Atrazine in 82% (maximum concentration 5 µg/L, rank 1) of all surface water samples. Particularly exposed streams (White river, Indiana), can temporarily reach very high concentrations in the order of 10 to 50 µg/L. These high concentrations are observed in a seasonal pattern (10 µg/L) due to non-restricted use and can reach exceptionally even higher values. (Tedesco et al. 2009).

In Germany Atrazine is banned since 1991 (Schmidt in Litz et al. (Ed.) 2003), in France the use of Atrazine was forbidden since 2003 (Reuters France 2001). Nevertheless Atrazine and its metabolites (DEA) are still detected in German (rank 2 and 7 (DVGW 2006 in Tedesco et al. 2009)) and French (rank 4 and 3 (IFEN 2006 in Tedesco et al. 2009)) surface waters due to its persistence in the environment and to its legal application (or later ban) in neighbouring countries (e.g., Switzerland). Moreover, concentration patterns in surface waters indicate significant illegal use (pers. comm. M. Bach 2009).

Groundwater

In an UBA study between 1990 and 2006, Atrazine and its main metabolite Desethylatrazine led the list of the herbicides which were detected most frequently above 0.1 µg/L in German shallow groundwaters. However, the tendency of their occurrence is decreasing from 2.2% of 12353 sampling sites between 1996 and 2000 to 1.78% of 4496 sampling sites in 2006 (UBA 2009).

In 1995, Atrazine and Desethylatrazine were at the top of the French herbicide list by exceeding the threshold of 0.1 µg/L in the most groundwater sampling sites (2.85 % of 27466) (Isenbeck-Schröter et al. 1998). The same trend can be observed in 2006 (IFEN) for DEA and Atrazine (rank1 and 2) with respectively 32 and 22 % (detected/analysed).

In a survey all over the USA from 1992 to 2001, Atrazine was detected in approximately 13% of all searched groundwater bodies under agricultural land use areas with concentration more than or equal to 0.1 µg/L. (Gilliom 2006)

Drainage water

In literature it could be found a wide range of Atrazine concentrations in drainage water of agricultural used areas varying between 0.004 µg/L (Kronvang et al. 2003) and 120 µg/L (Warnemünde et al. 2007). The 25%- and the 75%-quantile of the researched concentrations are 0.48 µg/L and 16.95 µg/L, respectively.

2.1.4 Treatability in drinking water plants

The removability of Atrazine from source water with classical drinking water treatment techniques (flocculation, filtration, ozonation) have to be classified as non-sufficient, because less than 50 % can be eliminated. With an additional attempt using powdered activated carbon (PAC) more than 50% of the remaining substance can be removed. (pers. comm. P. Roche 2009)

Kingsbury et al. (2008) examined finished drinking water of 9 US water works and found Atrazine in 87 % of all samplings with maximum concentration of 3.4 µg/L (rank 2).

2.1.5 Toxicity / Regulatory thresholds

In Europe the legally enforceable threshold for all pesticides in source waters is 0.1 µg/L for single substances and 0.5 µg/L for the sum of pesticides plus metabolites (European Drinking Water Directive, 98/83/EEC). This threshold is defined for a single exceedance. In the USA there is a legally enforceable drinking water standard, maximum contaminant level (MCL) for Atrazine of 3 µg/L (Kingsbury 2008). In contrast to the EU legislation, the MCL must not be exceeded by annually averaged concentrations with specific rules regarding the sampling timing and frequency

Published values for the acceptable daily intake (ADI) of Atrazine vary depending on the recommending institution from 0.005 mg/kg/day (BfR 2003) to 0.02 mg/kg/day (WHO 2007). The Reference Dose (RfD), which describes the maximum daily amount of a chemical that a human body can absorb without experiencing chronic health effects and which is based on a more rigorously defined methodology is 0.035 mg/kg/day (EXOTOXNET 2009). The acute reference dose (ARfD), which describes the amount of a chemical that a human body can absorb without experiencing acute health effects is 0.025 mg/kg/d (BfR) and 0.1 mg/kg/d (WHO) (BfR 2006).

The acute oral lethal dose (LD_{50}) for rats is 1869 mg/kg (moderate). US EPA classifies Atrazine as slightly toxic for humans. (PPDB 2009)

According to the WHO, Atrazine is unlikely to present acute hazard in normal use (EXOTOXNET 2009). Carcinogen, endocrine and neurotoxic effects are suspected, but this status remains unconfirmed (PPDB 2009). In recent researches in the USA low birth weight and birth defects of babies are tied to Atrazine exposure. This is leading to a rereview of Atrazine registry in the USA by the USEPA (pers. comm. Leonore Tedesco 2010). Atrazine causes no mutagenic or teratogenic activities (Schmidt in Litz et al. (Ed.) 2003). Bioaccumulation of Atrazine is not environmentally important (EXOTOXNET 2009). A transfer of phyto-toxic effects to the next season due to plant residues in soil is possible. (Schmidt in Litz et al. (Ed.) 2003)

Toxicity for aquatic organisms is moderate (Fish (Oncorhynchus mykiss) - (Acute 96 hour LC_{50}): 4.5 mg/L, Aquatic invertebrates (Daphnia magna) - (Acute 48 hour EC_{50}): 85 mg/L, Algae (Raphidocelis subcapitata) - (Acute 72 hour EC_{50}, growth): 0.059 mg/L) (PPDB 2009). The USEPA has aquatic community guidelines of 2003 for both acute and chronic exposures: Acute toxicity - vascular plant : 18 µg/L, Acute toxicity - nonvascular plant: 32 µg/L, Chronic toxicity - invertebrate: 62 µg/L, Acute - toxicity invertebrate: 360 µg/L, Chronic toxicity fish: 62 µg/L and Acute toxicity - fish: 2650 µg/L.

2.1.6 Metabolites

The main metabolites of Atrazine are dealkylized Atrazines mainly produced by microbiologically catalyzed processes and hydroxylized Atrazines, mainly produced by hydrolysis. Microbiological degradation is favoured by neutral pH values. The influence of abiotic chemical reactions become dominant under more alkalic or acidic conditions. (Schmidt in Litz et al. (Ed.) 2003)

The dealkylized Atrazines DesethylAtrazine (DEA) and DeisopropylAtrazine (DIA) are the most relevant metabolites.

- DesethylAtrazine (Ref: G-30033) (DT_{50}: 45d (moderately persistent), GUS leaching index: 3.54 (highly leachable), K_{oc}: 72 mL/g (mobile), Rat (LD_{50}): 464 mg/kg (moderate), Algae (Acute 72 hour EC_{50}, growth): 0.1 mg/L). (PPDB 2009)
- 6-DeisopropylAtrazine (DT_{50}: n.d., GUS leaching potential index: n.d., K_{oc}: 142 mL/g (moderately mobile), Rat (LD_{50}): n.d.))

One of the major metabolites, Desethylatrazine, was detected in 79.3 % of the examined US streams (rank 3 of the most frequently detected conventional pesticides) and in 12 % with concentrations above 0.1 µg/l (rank 4) by Gilliom et al. (2006). In a more recent study (2004-2005) in the USA Kingsbury et al. (2008) found the metabolites Desethylatrazine, Deisopropylatrazine and 2-Hydroxyatrazine in 58% (max. conc. 0.13 µg/L, rank 7), 58% (max. conc. 0.09 µg/L, rank 7) and 52% (max. conc. 0.38 µg/L, rank 10) of all examined source waters, respectively and in 68 % (max. conc. 0.13 µg/L, rank 3), 63 % (max. conc. 0.12 µg/L, rank 4) and 51% (max. conc. 0.3 µg/L, rank 10) of all examined finished waters, respectively.

In Germany Desethylatrazine and Deisopropylatrazine are listed on the 7th and the 21st place in the ranking based on detection frequency in German surface waters and on the 5th and the 31st place based on detection frequency in the River Rhine (Sturm et al. 2005).

In the UBA study of 2006, no German monitoring stations with concentrations > 0.1 µg/L were reported (UBA 2006 in Tedesco et al. 2009). In France, Desethylatrazine is in 3rd place in the ranking based on detection frequency in surface waters (IFEN 2006 in Tedesco et al. 2009), ranked just above its parent substance Atrazine.

2.2 Bentazone

The herbicide Bentazone has been on the market since 1972 (PPDB 2009). It is applied after plant emergence and used for selective control of broadleaf weeds and sedges (a weed) in sweet corn, beans, rice, corn, peanuts, mint and others. In Germany, Bentazone is most frequently used for cereals next to corn (Sturm et al. 2005). According to the French ministry of agriculture (2010) the herbicide is allowed to be used for a wide range of cultured plants, such as sweet corn, sorghum, rice, corn, soya, peas and different kinds of cereals (http://e-phy.agriculture.gouv.fr/mata/998.htm). Bentazone is a contact herbicide, which means that it affects only the parts of the plant to which it is applied. It interferes with the ability of susceptible plants to use sunlight for photosynthesis. (EXOTOXNET 2009).

2.2.1 Chemical and physical parameters

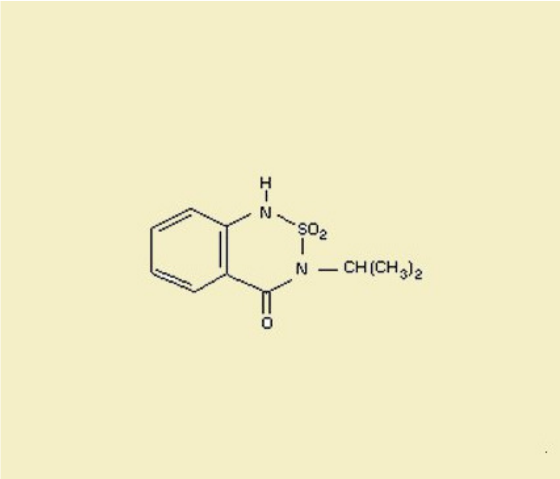

Fig. 2: Molecular structure Bentazone (PPDB 2009)

Bentazone (3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide) is highly soluble in water (570 mg/L at pH 7 and 20℃, (500 mg/L at 20℃, EXOTOXNET 2009) and barely volatilizes (K_{HENRY}: 7,2 x10^{-5} Pa m^3/mol (25℃)). Still, a drift of the substance to non-target areas via aerosols due to application methods, like spraying has to be anticipated (Reichenberger 2006). The distribution coefficient between Octanol and water (logKow) is low (-0.46 (pH 7, 20℃)). The dissociation constant of Bentazone in water is 3.28. The sorption on soil is low (average K_{OC}: 51 mL/g, (34 mL/g, EXOTOXNET 2009, 13-176 mL/g, Sturm et al. 2005)). Boivin et al. (2005) found a negative correlation between Bentazone adsorption to soil and natural (5.3 -8.2) soil pH-values. He assumed that higher desorption rates of Bentazone, compared to other herbicides like Atrazine, could be connected to weaker interactions of the molecule to soil components. On the contrary, Knauber et al. (2000) reported on the formation of bound residues (= strong connections) of Bentazone in humic substance depending on microbial activity, which was stimulated by the presence of oxygen; however, there was also a significant immobilization of Bentazone in the absence of oxygen.

Bentazone is characterised by a low persistence against microbiological transformation in aerobic soil (typical DT50: 13d (35d, aerobic soil, Gilliom 2006)). Field experiments resulted in comparable half life values (DT50: 14d, range 4 – 21d). (PPDB 2009)

The mineralisation (= complete breakdown of molecule) rate of Bentazone is quite low and given with 6-9% in 90 days (European Commission 2000). Knauber et al. (2000) observed that under anoxic conditions, the mineralization activity was less than 5% of the activity under aerobic conditions. Microbiological breakdown in water is lower than in soil (DT_{50}: 161d, Sturm et al. 2005, >200d, Gilliom et al. 2006). Moreover, Bentazone appears to be stable to hydrolysis. However, it has a comparably low half-life in surface water because it is readily broken down by sunlight (photolytic half life: < 24h, EXOTOXNET 2009; 122 h at pH 5 and 63 to 93 h at pH 7, Sturm et al. 2005).

Bentazone has the potential to contaminate surface water via run-off water from treated crops because of its high mobility. This characteristic of Bentazone also suggests a strong potential for groundwater contamination. However, its breakdown by photolysis above ground and its rapid degradation by soil bacteria and fungi in unsaturated soil are expected to prevent significant contamination of groundwater (EXOTOXNET 2009)

According to the GUS leaching potential index, Bentazone is a marginal leacher (2.55, PPDB 2009, 2.62, Papa et. al. 2004) or a leacher (3.22, Gan 2002).

2.2.2 Analytical methods

Bentazone can easily be removed from water by solid phase extraction (Vink et al. 1996). It has to be derivatized (methylated) (Gaynor et al. 1981) and can be analysed by GC/MS. In the ISO method 15913, the DIN method 38407-20 as well as in the US EPA method 515.2 (Determination of Chlorinated Acids in Water using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector) a standard procedure is published to allow international reproducibility of the analytical attempt. From soil, Bentazone has to be extracted by methanol (Thorstensen & Lode 2001).

Due to its structure, it would be possible to quantify Bentazone alternatively by HPLC/UV instead of GC/MS, however detection limits are higher and selectivity is lower.

In France (CAE) Bentazone is analysed by HPLC/MS/MS (pers. comm. P. Roche 2010). The selectivety of this detection method is higher compared to HPLC/UV.

2.2.3 Trends of use/ trends in concentration in surface waters and groundwater

Use

In the USA, Bentazone is applied in comparably low quantities, predominantly for specific plants. In particular, it is used on 5 % and 23 % of all fresh and processing sweet corn fields, respectively (US EPA 2003).

The most recent figures of use are: 1987 (6-9 million lbs., rank 15), 1993 (4-7 million lbs., rank 18), 1995 (4-8 million lbs., rank 23) and 1997 (6-8 million lbs., rank 21). From 1999 to 2001 it was no longer listed in the ranking of the 25 most important conventional pesticides, because of the increased use of other products and a slightly decreased use of Bentazone. (Kiery 2004)

Bentazone is used all over Europe except in Romania and Malta (PPDB 2009). In Brandenburg (German state) the sales figures were stable from 1998 to 2003 (around 30 tons per year). In 1999, Bentazone was the 5th most used herbicide in Brandenburg. In 2001 and 2003 it was in the 6th position (LUA Brandenburg 2003). Sturm et al. (2005) report that in 2005, 250 to 1000 t of Bentazone were sold in Germany and that Bentazone is usually applied at a rate of 0.75 kg/ha/yr (corn) and 1 kg/ha/yr (cereals).

Surface water

In a US stream survey between 1992-2001 by Gilliom et al. (2006), Bentazone was listed on rank 11 of the most frequently detected conventional pesticides (found in 16.3 % of all examined surface waters) and on rank 6 of the most frequently detected conventional pesticides with concentrations above 0.1 µg/L (found in 7.6 % of all examined surface waters). These high rankings cannot be explained by high use (see above), but probably because of the high mobility of Bentazone. In a more recent study (2004-2005) in the USA, Kingsbury et al. (2008) found Bentazone in 18% of all examined surface waters with a maximum concentration of 0.2 µg/L (rank 21). The different ranking is the result of the inclusion of a great number of metabolites, not measured by Gilliom et al. (2006). If the additionally measured substances are neglected, Bentazone is on rank 8 in the study by Kingsbury et al. (2008).

Bentazone is listed in the 9th place in the ranking based on detection frequency in German surface waters (Sturm 2005). The Percentage of German monitoring stations with concentrations > 0,1 µg/L was < 10 % (UBA 2006 in Tedesco et al. 2009). In France, Bentazone is in the 11th place in the ranking based on detection frequency in surface waters (IFEN 2006 in Tedesco et al. 2009).

Groundwater

In a survey covering the entire USA from 1992 to 2001, Bentazone was detected at concentrations ≥ 0.1 µg/L in approximately 2.5% of all examined groundwater bodies under agricultural used areas (rank: 8.) (Gilliom et al. 2006).

In a UBA study between 1990 and 2000, Bentazone climbed from the 9th to the 4th position in the list of the most detected herbicides above 0.1 µg/L in German shallow ground waters. In 2006, Bentazone was displaced from 4th to 5th position, however its occurrence has decreased barely from 0.82 % of 8578 sampling sites between 1996 and 2000 to 0.77 % of 3769 in 2006.

In 1995, Bentazone was in the 6th rank of the French herbicide list, exceeding the threshold of 0.1 µg/L in ground water sampling sites (0.09 % of 8524) (Isenbeck-Schröter et al. 1998).

Drainage water

A literature review showed a wide range of Bentazon concentrations in drainage water of agricultural used areas varying between 0.002 µg/L (Kronvang et al. 2003) and 100 µg/L (Larson & Jarvis 1999). The 25%- and the 75%-quantile of the researched concentrations are 2.75 µg/L and 80 µg/L, respectively.

2.2.4 Treatability in drinking water plants

The removability of Bentazone from source water with classical drinking water treatment techniques (flocculation, filtration, ozonation) is comparably good, because more than 90 % can be eliminated. This compound is very reactive to ozone. With additional use of powdered activated carbon (PAC) more than 50% of the remaining substance can be removed. (pers. comm. P.Roche 2009)

Despite good removability, Bentazone is listed in 1st place regarding occurrences in finished drinking water in Baden-Württemberg (German state, mostly groundwater/bank filtrate) (Ammon 2006 in Tedesco et al. 2009).

Kingsbury et al. (2008) examined finished drinking water of 9 US water works and found Bentazone in 16% of all samplings with maximum concentration of 0.2 µg/L (rank 17 or rank 7 without metabolites).

2.2.5 Toxicity / Regulatory thresholds

In Europe, the legally enforceable threshold for all pesticides in source waters is 0.1 µg/L for single substances and 0.5 µg/L for the sum of pesticides plus metabolites (European Drinking Water Directive, 98/83/EEC).

In the USA, there is no legally enforceable drinking water standard, like maximum contaminant level (MCL) for Bentazone. However, the U. S. Geological Survey (USGS), in cooperation with US EPA, developed a legally non-enforceable health-based screening level (HBSL) of 200 µg/L for Bentazone, which is advised to supplement the missing maximum contaminant level (MCL) for water quality management. (Cook 2007, Kingsbury 2008)

The acceptable daily intake (ADI) is 0.1 mg/kg/day (BfR 2006). The Reference Dose (RfD), which describes the maximum daily amount of a chemical that a human body can absorb without experiencing chronic health effects and is based on a more rigorously defined methodology yields between 0.0025 mg/kg/day (EXOTOXNET 2009) and 0.03 mg/kg/day (US EPA - IRIS 1998). The acute reference dose (ARfD), which describes the amount of a chemical that a human body can absorb without experiencing acute health effects is 0.25 mg/kg/d (BfR 2006).

The acute oral lethal dose (LD50) for rats is 500 mg/kg (moderate). Bentazone is slightly toxic for humans according to US EPA or slightly hazardous according to WHO. No carcinogen, endocrine reproduction/development and neuro-toxicant effects are known. (PPDB 2009)

Bentazone has a low potential to accumulate in fauna. Toxicity for aquatic organisms is moderate (Fish (Oncorhynchus mykiss) - (Acute 96 hour LC_{50}): 100 mg/L, Aquatic invertebrates (Daphnia magna) - (Acute 48 hour EC_{50}): 64 mg/L, Algae (Lemna gibba) - (Acute 72 hour EC_{50}, growth): 10.1 mg/L). (PPDB 2009)

Crops may be harmed if Bentazone is applied to plants that have been subjected to stress, such as drought or high temperature fluctuations (EXOTOXNET 2009).

2.2.6 Metabolites

According to the Directive 91/414 EEC, Bentazone has no known relevant metabolites; this signifies that (i) the known metabolites have no comparable intrinsic properties to the parent chemical in terms of its biological target activity, and (ii) the known metabolites have no toxicological properties that are considered severe, and (iii) the known metabolites do not pose a higher or comparable risk to organisms than the parent substance (PPDB 2009). A minor metabolite is 2-amino-N-isopropylbenzamide (DT_{50}: n.d., GUS leaching index: n.d., K_{OC}: 155 (moderately mobile), Rat (LD_{50}): n.d.).

6-hydroxybentazone and 8-hydroxybentazone are also mentioned in literature but data on their concentration in water are lacking.

Chapter 3
Experiences in mitigation systems

The following chapter provides a review on pesticide behaviour in near-natural mitigation zones or similar systems, with a clear focus on Atrazine and Bentazone. Generally, only few studies exist on pesticide removal in near-natural mitigation zones; the focus in comparable studies being often on nutrients only.

3.1 Wetlands and buffer strips

The elimination potential of Atrazine in constructed wetlands is negatively correlated to flow velocity and therefore residence time. Input concentration reduction reached from 25 % (4.9 cm/d) to 95 % (1.5 cm/d) (Kadlec & Hey 1994). Anderson et al. (2002) observed biotic Atrazine mineralization between 60 and 80% per month in constructed wetlands (hydraulic residence time: 4-21 days; input conc. 13 µg/L). Moore et al. (2000) applied comparatively high Atrazine input concentrations (73 and 147 µg/L) to constructed wetlands and simulated a rain storm event (3-fold volume exchange) shortly after application to evaluate sufficient wetland dimensions for Atrazine reduction to 20 µg/L by transfer and transformation processes (only water samples were taken). The identified required residence times were 30 - 39 days and 133 – 143 days for the two concentration levels, respectively.

Anderson et al. (2002) identified the responsible processes mostly at the well oxidized top five cm of the wetland sediment. Detenbeck et al. (1996) referred to previous investigators (Wang et al. 1991) who have demonstrated that the carboxylic groups in humic acids of organic sediments (and presumably plant litter) are responsible for binding Atrazine and catalyzing chemical hydrolysis to Hydroxyatrazine. He observed half lives of 8 – 14 days in constructed wetlands with flow velocities of 76 L/min. Boivin et al. (2005) examined the sorption of Atrazine in soils. They have found positive correlation between Atrazine adsorption and the content of organic matter. Gosh (2003) referred to Struthers et al. (1998) who affirmed enhanced degradation rate of Atrazine under aerobic conditions when external carbon sources were supplied to pure bacterial culture. Douglass & Tuovinen (2005) acheived higher mineralization rates of Atrazine under aerobic than under anaerobic conditions in constructed wetland sediments. After 70 days, 25% of radioactive labelled CO_2 evolved in the presence of oxygen in contrast to 12 % in the absence of oxygen. However, Crawford et al. (1998) observed the transformation of 50% of Atrazine into Hydroxyatrazine within 144 h under denitrifying conditions. The degradation of Atrazine to Hydroxyatrazine is usually slower (anaerobic conditions), but should be preferred because this metabolite is less toxic than metabolites such as DEA or DIA, which are formed under aerobic conditions. Chung et al. (1996) examined Atrazine degradation in anaerobic wetland sediment and could report an increase of Hydroxyatrazine formation by adding external organic carbon. In 38 weeks, 20 % and 43% were transformed without and with addition of glucose,respectively.

Further, Anderson et al. (2002) referred to studies of Ro & Chung (1995) who observed a decrease in Atrazine concentration in spiked wetland sediment samples from 10 mg/L to

<10 µg/L within 10 weeks under aerobic conditions; subsequent spikes were depleted in 3 weeks. Runes et al. (2001) could confirm that adaption or bioaugmentation (= addition of adapted microorganisms) with Atrazine degraders increases mineralization. Runes further showed that plant cover in wetlands promotes survival of Atrazine degraders during the absence of Atrazine.

Atrazine in particle bound (runoff) and diluted form (subsurface flow) can also be reduced substantially by vegetated buffer strips and riparian zones. Hall et al. (1983) found Atrazine reduction in runoff water from 65 % to 91 % of application rates from 4.4 and 2.2 kg/ha, respectively, in 6m wide oat-covered strips. Schulz et al. (1994) observed Atrazine reductions in runoff water of 55% and 92% from starting concentration of 4 ppb and 2.6 ppb, respectively, in vegetated strip sequences, planted in order of flow direction with grass, shrub and trees (total width: more than 7m). The infiltration potential is the decisive factor of Atrazine reduction in runoff. Buffer strips intercept Atrazine also in subsurface flow. Hoffman (1995) experimented with 9m wide vegetated buffer strips covered with bermuda grass and wheat and observed 57% and 30% reduction, respectively. Hatfield (1995) examined adsorption of Atrazine to soil and organic matter and confirmed that 20% of Atrazine applied on a maize field wasn't only being infiltrated but trapped within a 20m grass buffered strip. He assumed that reduction of Atrazine in the top 2cm of the buffer in the following season was linked to degradation. (Baker et al. 1995)

Lin et al. (2005) observed enhanced degradation of Atrazine in vegetative buffer strips due to organic matter and therefore higher enzymatic activity. Moore et al. (2001) observed the important role of vegetation in drainage ditches to mitigate wash out of Atrazine, which is sorbed to the plant matrix during runoff events.

The effectiveness of these mitigation systems is strongly dependent on water flow over and across the buffer. Problematic is the decrease of reduction potentials, in the case that the buffer strips have to be bypassed by tiles and drainage pipes during strong rainfall events, because of insufficient hydraulic capacities.

Studies on the behaviour of Bentazone in mitigation facilities are much scarcer. No information on Bentazone in constructed or natural wetlands was found. However, Conger and Portier (1997) assessed the phyto-remediation potential of different tree species, which could be applicable in buffer strips. They found that Bentazone is well absorbed by special phreatophytes (= fast growing trees with high transpiration rates, e.g. black willow) via their roots and transported to the canopy, where it is degraded by photolysis to lower order derivative compounds without harming the plant (if the concentrations do not exceed the tolerance level of the plant). Mineralisation rates of 19% to 27% were observed in single plant experiments with a Bentazone dosing of 150 mg/L/d during 3 weeks.

3.2 Biobeds and Biopurification Systems

Biobeds are quite new technical systems to prevent herbicide contamination of the environment from point sources, such as cleaning sites for farming machines and herbicide application devices as well as contaminated discharges from herbicide storage and handling sites. Biobeds are usually filled with layers of different organic materials such as straw, peat, coco fibres or garden waste compost. The contaminated liquid percolates vertically with relatively high residence times in the order of days/weeks/months under aerobic to anoxic conditions. (Castillo et al. 2008)

In quite high concentrated experiments Castillo et al. (2000) observed degradation of Bentazone (dosing: 10 mg/L) in straw-filled bioreactors (circulated flow) with nitrogen additions related to the enzyme production of the white rot fungus. No and low nitrogen addition (35 mg/L N) gave high loss of straw and rapid Bentazone degradation (80 -105 µg/d) during a period of 31 days (degradation rate: 25% - 33%). Higher nitrogen addition (175 mg/L N and 350 mg/L N) resulted in lower degradation (16 - 17 µg/d / 5%). In 2001, Castillo et al. observed a decrease of 65% of Bentazone in 20 days, which coincided with the presence of the activity of the lignin degrading enzymes; lignin- and manganese peroxidise. However, the influence of these enzymes on Bentazone degradation is not completely clarified. Information on Atrazine degradation in biobeds are not available, probably due to its ban in Europe, where the beginning of research on biobeds is located. Still, comparable substances from the triazine family, like Therbuthylazin and Cyanazin could be reduced successfully (95 % after 1 year) (Castillo et al. 2009).

De Wilde et al. (2009) tested the sorption of Bentazone among other herbicides on various materials with high organic carbon content, such as straw, peat mixture, cocos chips, garden waste compost and willow chopping and found that Bentazone was best adsorbed to peat mixture and coco chips and to a medium extent to straw (K_{OC}: 6 L/kg).

3.3 Biotrenches and instream reactors

Biotrenches are ditches, filled with organic material, predominantly used to reduce nutrient loads from drainage water. In the USA, in the Santa Clara River region, a project is running at the University of California, Santa Barbara with the scope to asses the performance of biotrenches for the treatment of agriculture runoff. They used straw to serve as a growth medium for biofilms and examined mainly nutrient reduction. The groundwater quality was the primary form of assessment (pers. comm. Kristin Clark). In the Midwest of the USA, trenches filled with woodchips as organic carbon sources were tested successfully in the field to reduce nutrients.

Robertson and Mercley (2008) could affirm the positive influence of woodchips on nitrate reduction conducting experiments with so called in-stream reactors, which are designed comparable to filled trenches.

3.4 Summary of existing experiences

The sorption of Atrazine and Bentazone on soils is moderate. Moderate sorption in combination with medium to high persistency makes these compounds quite mobile, so they can usually be observed in surface waters in general and in ground waters near places of their application. First experiences show that mitigation systems can be effective measures to decrease their concentrations by supporting biotic and abiotic dissipation processes, mainly at high residence times.

Adding organic matter can improve adsorption of Atrazine and Bentazone, an important dissipation process in these systems. Degradation rates for Atrazine and for Bentazone can be increased by implementing highly microbiologically active conditions which can usually be accomplished in the presence of external carbon sources. While mineralization of both herbicides is favoured in aerobic environments; however significant degradation of Atrazine was also observed under anaerobic conditions.

A great number of open questions remain on how to design a mitigation system, which is adequate to reduce herbicides in drainage water. For instance, there is no specific information on the degradation of diluted and adsorbed forms of the herbicides, very little information about necessary residence times, adsorption constants, half lives and leaching behaviour in specific substrates or comparable designs. Moreover, the influence of nitrogen, which is present in drainage water at high concentrations, on degradation of Atrazine and Bentazone remains uncertain. Finally, the behaviour of Atrazine and Bentazone (contained in agricultural drainage water) in mitigation systems in general and in bioretention swales in particular is poorly studied.

Chapter 4

Implications for Aquisafe 2

The literature study clarifies the high mobility and the high use of Atrazine and Bentazone which leads to a relevant negative impact on the environment and drinking water production. There is a need for efficient and cost-effective reduction measures such as mitigation systems, which are located near the sources. So far the behaviour of Atrazine and Bentazone in existing mitigation systems is poorly studied. Two main goals of Aquisafe 2 are (i) the improvement of the knowledge on the dissipation potential of existing mitigation systems for herbicides and (ii) the development of designs for practicable advanced solutions, with focus on bioreactive swales.

Realistically, mitigation systems would only be implemented if they also allow significant reduction of nitrates, which are often the primary concern.

Both for nitrates and herbicides, the presence of external organic carbon sources (with a combination of fast accessible and sustainable substrate partitions) is presumed to be the basis for dissipation processes and effective reduction.

Reese & Griesbach (1996) in Rolf (2002) favour bark mulch as sustainable organic carbon source for effective denitrification (80%). Straw has also a high potential (>90%) because of its fast accessible organic carbon (Witz 2005).

These substrates also promise a good base to establish highly active communities of microorganisms capable to degrade herbicides. Adsorption is also a very important dissipation process and a tool to decrease herbicide discharge effects on the environment, above all by lowering the peak concentrations and supporting degradation by increasing residence time. Adsorption potential of straw and bark mulch regarding Atrazine and Bentazone is moderate. But stronger adsorbing materials, such as peat or coco fibres, would be less effective for denitrification, more expensive and/or less permeable.

A prior challenge of Aquisafe 2 is finding materials with sufficient permeability to avoid the bypassing of non-treated water volumes due to insufficient hydraulic capacity and to assure hydraulic residence times for sufficient degradation. Straw and bark mulch seem to be adequate. To figure out optimal residence times for substance dissipation it will be necessary to observe the herbicide and nitrate behaviour under a range of filtration velocites.

Next to adequate residence times the design of mitigation systems in agricultural areas is challenged, as mentioned, by the parallel need for reducing nitrate. Denitrification is restricted to low oxygen, denitrifying conditions, while the selected herbicides are predominantly degraded under aerobic conditions. Given the existing knowledge, systems using organic sources with aerobic and anoxic zones may be difficult to implement. Laboratory experiments show that because of high microbiological activity in organic carbon donating materials it is difficult to adjust zones of oxygen even with complex and costly constructions, such as aerators. Tests are suggested, whether the fluctuation of dry and saturated conditions in the swales as a result of seasonal variations in drainage discharge and corresponding entrance of air during dry periods can have measurable effects on the herbicide degradation performance.

The study of published agricultural drainage water contents shows a wide range of Atrazine and Bentazone concentrations depending on application practice, soil structure and soil composition. The concentrations in the wetland and buffer strip studies lie within this range. For the technical experiments in the WP 5 of Aquisafe 2 Atrazine and Bentazone are planned to be dosed in the range of 10 to 20 µg/L and 10 to 50 µg/L, respectively.

Concluding bioreactive swales filled with straw and bark mulch could be an adequately permeable and sufficiently organic carbon donating option with moderate herbicide adsorbing potential to reduce both nitrate and Atrazine/Bentazone concentrations and lower the negative impact on the environment and drinking water production.

Appendix

Comparative overview of the most relevant herbicide properties

A.1 Chemical and physical parameters

Tab. 2: Comparison of chemical and physical parameters

Properties[‡]	Unit	Atrazine	Bentazone
Mobility			
Solubility	mg/L	33 at 22°C	570 at 20°C
K_{OC}	mg/L	39 - 155	13 - 176
Persistence			
DT_{50} in aerobic soil	d	35 - 146	13 - 45
DT_{50} in anaerobic soil	d	105 - 200	degradation strongly reduced
DT_{50} in water	d	n.d.	161 - 200
Mineralisation	%	n.d.	6 - 9% (in 90 d)
Summary parameter (based on K_{OC} and DT_{50})			
GUS leaching index[‡‡]	-	3.6 - 3.75	2.55 - 2.62

[‡] see glossary in section four for definition of values

[‡‡] >1.8 – non-leacher, >1.8 and <2.8 marginal leacher, >2.8 leacher

A.2 Toxicity/Thresholds

Tab. 3: Comparison of toxicity and thresholds

Properties[‡]	Unit	Atrazine	Bentazone
Toxicity			
LD_{50} (Rat)	mg/kg	1869	500
LC_{50} (Fish)	mg/L	4.5	100
LC_{50} (Aquatic invertebrate)	mg/L	85	64
LC_{50} (Algae)	mg/l	0.059	10.1
Thresholds			
ADI	mg/kg/d	0.005 - 0.02	0.01 - 0.1
RfD	mg/kg/d	0.035	0.0025 - 0.03
ARfD	mg/kg/d	0.025 - 0.1	0.25
US MCL	µg/L	3	-
US HBSL	µg/L	-	200

[‡] see glossary in section four for definition of values

A.3 Trends of use/ trends in concentration in surface waters and groundwater

Tab. 4: Comparison of trends in use and in concentrations in source waters

Properties / Country	Unit	Atrazine	Bentazone
Use			
US sales (1987-2001)	Rank	1. – 2.	15. – n. d.
	tons/yr	ca. 40.000	3.000 – n. d.
Sales in Brandenburg (Germany) (1998- 2003)	Rank	not used	5. – 6.
	tons/yr	not used	ca. 33
Sales in Germany (2005)	tons/yr	not used	250 - 1000
Application dose	kg/ha	0.4-4.5	0.75-1
Detection frequency in surface waters			
USA (1992-2001)	Rank	1.	11.
	%[‡]	90,2	16.3
USA (2004-2005):	Rank	1.	21.
	%	82	18
Germany	Rank	2.	9.
Germany (River Rhine)		3.	11.
France		4.	11.
Detection frequency in ground waters[‡‡]			
USA (2001)	Rank	1.	6.
	%	2.85	0.09
Germany (2006)	Rank	1.	5.
	%	1.78	0.77
France (1995)	Rank	1.	8.
	%	13%	2.5

[‡] percentage of examined waters

[‡‡] more than or equal to 0.1 µg/L

A.4 Treatability in drinking water plants

Tab. 5: Comparison of treatability in drinking water plants

Property / Country	Unit	Atrazine	Bentazone
Classical treatment (filtration, flocculation, ozonation)			
Removal	%	< 50	> 90
Detection frequency in finished drinking water			
USA	Rank	2	17 (without metabolites: 7)
Germany (Baden-Württemberg)	Rank	-	1

A.5 Metabolites

Tab. 6: Comparison of the metabolites

Properties	**Unit**	**Atrazine**		**Bentazone**
Relevant metabolites	-	Desethyl-Atrazine	Deisopropyl-Atrazine	2-amino-N-isopropyl-benzamide
Persistence and mobility				
Typical DT50	d	45	n.d.	n.d.
K_{OC}	mL/g	72	142	155
GUS leaching index	-	3.54	n.d.	n.d.
Toxicity				
Rat LD_{50}	d	464	n.d.	n.d.
Fish LC_{50}	mg/L	n.d.	n.d.	n.d.
Aquatic invertebrate LC_{50}	mg/L	n.d.	n.d.	n.d.
Algae LC_{50}	mg/L	0.1	n.d.	n.d.
Detection frequency in surface waters				
US(1992-2001	Rank	3.	n.d.	n.d.
	%‡	79	n.d.	n.d.
USA 2004-2005):	Rank	7.	7.	n.d.
	%	58	58	n.d.
Germany	Rank	7.	21.	n.d.
Germany (River Rhine)	Rank	5.	31.	n.d.
France	Rank	3.	n.d.	n.d.
Detection frequency in ground waters‡‡				
USA (2001)	Rank	2.	n.d.	n.d.
	%	11	n.d.	n.d.
Germany (2006)	Rank	1.	n.d.	n.d.
France (1995)	Rank	1.	n.d.	n.d.
Detection frequency in finished drinking waters				
USA (2004-2005)	Rank	3.	4.	n.d.
	%	68	63	n.d.

‡ percentage of examined waters

‡‡ more than or equal to 0.1 µg/L

Bibliography

Anderson K. L., Wheeler K. A., Robinson J. B. & Tuovineh O. H. (2002): Atrazine mineralization potential in two wetlands. Published in Water Research, Vol. 36, N°19, 4785-4794

Backer J. L., Mickelson S. K., Hatfield J. L., Fawcett R. S., Hoffman D. W., Franti T. G., Peter C. J. & Tierney D. P. (1995): Reducing herbicide runoff: role of best management practices. Published in Brighton crop protection conference – Weeds - Vol. 2

BfR - Bundesinstitut für Risikobewertung (2006): Grenzwerte für die gesundheitliche Bewertung von Pflanzenschutzmittelrückständen. Published in the World Wide Web (www.bfr.bund.de/cm/218/grenzwerte_fuer_die_gesundheitliche_bewertung_von_pflanzenschutzmittelrueckstaenden.pdf) (last information retrieval October 2009) (in german)

Bohuss I., Rekasi T., Szikora S., Barkacs K., Zaray G. & Acs E. (2005): Interaction of acetochlor and Atrazine with natural freshwater biofilms grown on polycarbonate substrate in lake Velence (Hungary). Published in Microchem. J., Vol. 79, 201-205

Boivin A., Cherrier R. & Schiavon M. (2005): A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. Published in Chemosphere Vol. 61, 668–676

Burgoa B. & Wauchope R.D. (1995): Pesticides in run-off and surface waters. Published in Environmental Behaviour of Agrochemicals, John Wiley & Sons Ltd

Castillo M. Del Pilar, Andersson A., Ander P., Stenström J. & Torstensson L. (2001): Establishment of the white rot fungus *Phanerochaete chrysosporium* on unsterile straw in solid substrate fermentation systems intended for degradation of pesticides. Published in World Journal of Microbiology and Biotechnology, Vol. 17, 627 - 632

Castillo M. Del Pilar, Ander P., Stenström J. & Torstensson L. (2000): Degradation of the herbicide Bentazone as related to enzyme production by Phanerochaete chrysosporium in two solid substrate fermentation systems. Published in World Journal of Microbiology & Biotechnology, Vol. 16, 289 - 295

Castillo M. Del Pilar, Torstensson L. & Stenström J. (2008): Biobeds for Environmental Protection from Pesticide Uses - A Review. Published in J. Agric. Food Chem., Vol. 56, 6206–6219

Castillo M. Del Pilar, Torstensson L. & Stenström J. (last update March 2009): Biobeds – a Swedish contribution to environmental protection from pesticide pollution. Published in the World Wide Web: http://www.mikrob.slu.se/ShowPage.cfm?OrgenhetSida_ID=7296 (last information retrieval October 2009)

Chung K.H., Ro K. S. & Roy D. (1996): Fate and enhancement of Atrazine biotransformation in anaerobic wetland sediment. Published in Wat Res, Vol. 30, Nr.2, 341-346

Conger R. M. & Portier R.J. (1997) : Phytoremediation experimentation with the herbicide Bentazone. Published in the Journal of Environmental Cleanup Costs, Technologies and Techniques, Vol. 7, Issue 2, 19-37

Cook K. (2007): Water Quality Benchmarks - The What's and Why's of Their Application. 2007 Western Region Pesticide Meeting. Published in the World Wide Web:

http://pep.wsu.edu/wrpm/07%20ppt/K_Cook_Water%20Quality%20Benchmarks.ppt (last information retrieval October 2009)

Crawford J. J., Sims G. K., Mulvaney R. L. & Radosevich M. (1998): Biodegradation of Atrazine under denitrifying conditions. Published in Appl Microbiol Biotechnol Vol. 49, 618-623

Douglass J. F. & Tuovinen O. H. (2005): Atrazine biodegradation potential in a created wetland. Published in the World Wide Web: https://kb.osu.edu/dspace/bitstream/1811/5905/1/%2804%29%202.15%20J.D.%20Atrazine.pdf (last information retrieval October 2009)

Detenbeck N. E., Hermanutz R., Allen K. & Swift M. C. (1996): Fate and effects of the herbicide Atrazine in flow-through wetland mesocosms. Published in Environmental Toxicology and Chemistry, Vol. 15, No. 6, pp. 937–946

Del Valle P. L. & Nelson, J. O. (1994): Evaluation of Atrazine soil extraction methods for the determination by enzyme immunoassay and gas chromatography. Published in Arch. Environ. Contam. Toxicol., 375-83

De Wilde T., Spanoghe P., Ryckeboer J., Jaeken P. & Springael D. (2009): Sorption characteristics of pesticides on matrix substrates used in biopurification systems. Published in Chemosphere, Vol. 75, 100–108

European Commission (2000): Review report for the active substance Bentazone (7585/VI/97-final). Published in Annex I of Directive 91/414/EEC

EXOTOXNET (The Extension Toxicology Network), University of California-Davis, Oregon State University, Michigan State University, Cornell University, and the University of Idaho, http://extoxnet.orst.edu (last information retrieval October 2009)

Gan J. (2002): Pesticide and Groundwater Quality. Published in PesticideWise by University of California, Riverside Cooperative Extension in the World Wide Web: http://www.pw.ucr.edu/textfiles/pesticidewisewinter2002.pdf (last information retrieval October 2009)

Gaynor J. D.& MacTavish D. C.(1981): Pentafluorobenzyl, (trifluoromethyl)benzyl and diazomethane alkylation of Bentazone for residue determination in soil by gas chromatography. Published in J. Agric. Food Chem. 20, 626-629

Ghosh P. K. & Philip L. (2003): Atrazine degradation in anaerobic environment by a mixed microbial consortium. Published in Water Research, Vol. 38, 2277–2284

Gilliom R. J., Barbash J. E., Crawford C. G., Hamilton P. A., Martin J. D., Nakagaki N., Nowell L. H., Scott J. C., Stackelberg P.I E., Thelin G. P. & Wolock D. M. (2006): Pesticides in the Nation’s Streams and Ground Water, 1992–2001. Published in The Quality of Our Nation’s Waters by U.S. Geological Survey

Isenbeck-Schröter M., Kofod M., König B., Schramm T., Bedbur E. & Mattheß G. (1998): Auftreten von Pflanzenschutzmitteln in Oberflächengewässern und im Grundwasser. Published in Grundwasser – Zeitschrift der Fachsektion Hydrogeologie 2/98 (in german)

IFEN (2009): Les pesticides dans les eaux - Données 2006. Institut français de l'environnement. Published in the World Wide Web: http://www.ifen.fr/acces-thematique/eau/les-pesticides-dans-leseaux.
html?taille=target%3D_self

Kadlec R.H. & Hey D. L. (1994): Constructed Wetlands for river water quality improvement. Published in Water Science Technology, Vol. 29, No. 4, 159 - 168

Kiely T., Donaldson D. & Grube A. (2004): Pesticides Industry Sales and Usage - 2000 and 2001 Market Estimates. Published by U.S. Environmental Protection Agency

Kingsbury J. A., Delzer G. C. & Hopple J. A. (2008): Anthropogenic Organic Compounds in Source Water of Nine Community Water Systems that Withdraw from Streams, 2002–05. Published in Scientific Investigations Report 2008–5208 by U.S. Geological Survey

Knauber W.-R., Krotzky A.J. & Schink B. (2000): Microbial Metabolism and Further Fate of Bentazone in Soil. Published in Environ. Sci. Technol., 34, 598-603

Kronvang B., Iversen H. L., Vejrup K., Mogensen B. B., Hansen A.-M. & Hansen L. B. (2003): Pesticides in Streams and Subsurface Drainage Water within Two Arable Catchments in Denmark: Pesticide Application, Concentration, Transport and Fate. Danish Ministery of the Environment. Published in Pesticides Research, Nr. 69

Larson, M. H. & Jarvis, N. J. (1999): Evaluation of a dual-porosity model to predict field-scale solute transport in a macroporous soil. Published in Journal of Hydrology, 215, 153–171

Lin, C. H., Lerch R. N., Garrett H. E., & George M. F. (2005): Incorporating forage grasses in riparian buffers for bioremediation of Atrazine, isoxaflutole and nitrate in Missouri. Published in Agroforestry Systems, Vol. 63, 91-99

LUA – Landesumweltamt Brandenburg (2003): Pflanzenschutzmittel in der Umwelt - Erhebung von Pflanzenschutzmittel-Wirkstoffmengen im Land Brandenburg 2003 - ein Vergleich zu 2001 und 1998/99. Published in Studien und Tagungsberichte des Landesumweltamtes, Band 51 (in german)

Moore M. T., Bennett I.R., Cooper C. M., Smith Jr. S., Shields Jr. F. D., Milam C.D. & Farris J. L. (2001): Transport and fate of Atrazine and Lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi delta, USA. Published in Agriculture, Ecosystems and Environment Vol. 87, 309 - 314

Moore M. T., Rodgers Jr. H. J., Cooper C. M. & Smith Jr. S. (2000): Constructed wetlands for mitigation of Atrazine-associated agricultural runoff. Published in Environmental pollution, Vol. 110, 393 – 399

Papa E., Castiglioni S., Gramatica P., Nikolayenko V., Kayumov O. & Calamari D. (2004): Screening the leaching tendency of pesticides applied in the Amu Darya Basin (Uzbekistan). Department of Structural and Functional Biology, University of Insubria, Italy. Published in Water Res., 38 (16), 3485-3494

PPDB (The Pesticide Properties Database), University of Hertfordshire, http://sitem.herts.ac.uk/aeru/footprint/en/index.htm (last information retrieval June 2009).

Reichenberger S., Bach M., Skitschak A. & Frede H.-G. (2006): State-of-the-art review on mitigation strategies and their effectiveness. Published within the Sixth Framework Programme (2002 – 2006)

Reuters France (2001): France orders withdrawal of Atrazine, herbicides. Published in the World Wide Web: http://www.calisafe.org/_disc1/10000008.htm (last information retrieval October 2009)

Robertson W. D. & Mercley L. C. (2009): In-stream bioreactor for agricultural nitrate treatment. Published in J. Environ. Qual., Vol. 38, 230–237

Rolf, F. (2002): Weitergehende Abwasserreinigung in kleinen Kläranlagen. Published in the World Wide Web: http://opus.kobv.de/btu/volltexte/2007/144/pdf/diss_rolf.pdf (last information retrieval October 2009)

Runes H. B., Jenkins J. J. & Bottomley P. J. (2001): Atrazine degradation by bioaugmented sediment from constructed wetlands. Published in Applied microbiology and biotechnology, Vol. 57, No. 3, 427 - 432

Schmidt B. (2003): Atrazine. Published in Bodengefährdende Stoffe (Litz N., Wilke W. & Wilcke B.-M.), Wiley-VCH Verlag, Germany (in german)

Spongberg A. L. & Ganliang L. (2000): Adsorption of Atrazine and Metolachlor in three soils from Blue Creek wetlands, Waterville, Ohio. Published in Sciences of Soils Vol. 5, No.1

Sturm S., Kiefer J. & Eichhorn E. (2005): Befunde von Pflanzenschutzmitteln in Grund- und Oberflächenwässern und deren Eintragspfade – Bedeutung für die Wasserwirtschaft und das Zulassungsverfahren, DVGW-Forschungsvorhaben W 1/02/05. Published by Technologiezentrum Wasser Karlsruhe (in german)

Tedesco L., Hall B. E., Barr R. C., Matzinger A., Morel-Fatio A. (2009): Diffuse trace contaminants with relevance for drinking water production in rural and semi-rural environments. Project report. Kompetenzzentrum Wasser Berlin. http://www.kompetenz-wasser.de/index.php?id=383&type=0&jumpurl=fileadmin%2Fuser_upload%2Fpdf%2Fforschung%2FAquisafe%2FKWB_Aquisafe_D_1_1_Aug_2009.pdf

Thorstensen C. W. & Lode O. (2001): Laboratory degradation studies of Bentazone, dichlorprop, MCPA and propiconazole in Norwegian soils. Published in J. Environ. Qual. 30, 947-953

Umweltbundesamt (last update January 2009): Grundwasserqualität. Published in the World Wide Web: http://www.umweltbundesamt-umwelt-deutschland.de/umweltdaten/public/theme.do?nodeIdent=2397 (last information retrieval October 2009)

US EPA (US Environmental protection agency) (2003): Interim Reregistration Eligibility Decision for Atrazine. Published in the World Wide Web: http://www.epa.gov/oppsrrd1/reregistration/REDs/Atrazine_ired.pdf (last information retrieval October 2009)

US EPA (US Environmental protection agency) (2003): Assessment of Potential Mitigation Measures for Atrazine. Published in the World Wide Web: http://www.btny.purdue.edu/ppp/ABA-02-03.pdf (last information retrieval October 2009)

US EPA – IRIS (US Environmental protection agency – Integrated risk information system) (1998): Bentazone (Basagran) (CASRN 25057-89-0). Published in the World Wide Web: http://www.epa.gov/iris/subst/0134.htm (last information retrieval October 2009)

Vink M. & Van der Poll J. M. (1996): Gas chromatographic determination of acid herbicides in surface water samples with electron-capture detection and mass spectrometric confirmation. Published in J. Chromatogr. A 733, 361-366

Warnemuende, E. A., Huang, C. & Bucholtz, D. (2007): Observed Atrazine and Glyphosate Losses in Agricultural Drainage Water at Various Watershed Scales. Paper presented at the annual meeting of the SOIL AND WATER CONSERVATION SOCIETY, Saddlebrook Resort, Tampa, Florida

Witz U. (2005): Festbettnitrifikation und –denitrifikation mit festen Kohlenstoffquellen – Biologische Stickstoffelimination in der Nachsorge von Deponien. Fachgebiet Abfall- und Siedlungswasserwirtschaft. Bergische Universität Wuppertal. Heft 4. Published in the World Wide Web: http://elpub.bib.uni-wuppertal.de/edocs/dokumente/fbd/bauingenieurwesen/diss2005/witz/dd0502.pdf