Atrazine in European groundwater

The distribution of Atrazine and its relation to the geological setting

Hanna Hertzman

Abstract

Atrazine has been banned for use in the European Union since 2004 but it is still one of the most frequently found pesticides in European groundwater. This literature review provides an insight of how and where Atrazine is contaminating groundwater across Europe. Many important factors have been stated to control the occurrence and fate of Atrazine in the receiving environment. The geological setting and the condition of the receiving environment in terms of pH, organic matter and/or clay content as well as the chemical and physical properties of the compound itself are controlling the transport through the subsurface towards the groundwater. The concentration levels range from 1,53 µg L^{-1} to 0,008 µg L^{-1}. The highest concentration was found while Atrazine was still in use, while the lowest concentration was found in Sweden where Atrazine has been banned since 1989. Eleven of the included investigations found concentrations above the threshold values given in the European Groundwater Directive. No general patterns could be seen when regards the vulnerability of the included types of aquifers it is rather a complex combination of contributing factors that influences the fate of Atrazine in the environment.

Key words: Atrazine, aquifer, groundwater contamination.

Table of content

1. Introduction and aim

A small percentage of water on Earth encompasses fresh water available for humans and ecosystems. More than 98 % of the fresh water constitutes groundwater (Fetter, 2001). Groundwater supplies ecosystems with water worldwide. It accounts for approximately half the world's potable water supply and it is important for industry and global food production. Therefore it is considered as one of the most important natural resources (WWAP, 2009). As described in the first paragraph in the Water Framework Directive stipulated by the European Parliament and Council: "Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such" (EU, 2000/60/EC).

The use of pesticides is an important way to protect plants against organisms that can harm them and their yield, but these chemicals can further involve risks to humans, ecosystems and the environment (Silva et al. 2012). The use of these chemicals has led to an environmental concern due to their potential runoff and leaching through the subsurface, thereby contaminating both surface and groundwater (Graymore et al. 2001). Contamination of groundwater due to the use of pesticides occurs worldwide and as the global population and food demand increases the contamination of groundwater is likely to continue into the foreseeable future (WWAP, 2009).

In the European Union the preservation of groundwater started to be promoted through the first directive developed in 1979: the Directive 80/68/EEC. The development of the type of legislation has led to today's Water Framework Directive, 2000/60/EC and the Groundwater Directive, 2006/118/EC (European Commission, 2016). These documents and the adjustments thereof have led to the development of environmental quality standards for pesticides, including relevant metabolites, degradation and reaction products in groundwater. The threshold value is set to 0,1 µg L^{-1} for individual substances and a total sum of pesticides at 0,5 µg L^{-1} (European Parliament and Council of the European Union, 2006/118/EC). Further developments of the directives have led to the Directive on Environmental Quality Standards (2008/105/EC), which includes a list of 33 priority substances, of these 13 substances are pesticides. One of the pesticides included in the priority list is Atrazine (here after, ATZ). ATZ is banned in the European Union since 2004 (Commission Decision, 2004/248/EC).

ATZ ($C_8H_{14}ClN_5$) is a member of the chemical group of pesticides called Triazines and was used against unwanted broadleaf weed plants and grasses and designed to disturb their photosynthetic mechanisms (Švorc et al. 2013). ATZ is an uncharged pesticide and considered as a mobile, stable and persistent substance in the environment and has a half-life time around 20-100 days.[1] It has a low reactivity, slow degradation and low water solubility (Kucka et al. 2012: Xing et al. 2012). When ATZ is released into the environment it can either remain chemically intact or it can degrade through physiochemical or biochemical processes into metabolites (Schocken and Speedie 1984; Radosevich et al. 1989). ATZ has four main metabolites that have been found in groundwater and surface water; deethyl-atrazine (DEA) deisopropylatrazine (DIA) and diamonochlorotriazine (DACT), and hydroxyatrazine (HYA) (WHO, 2010).

In a European wide survey on the occurrence of organic pollutants in groundwater, Loos et al. (2010) found ATZ to be the most frequently found pesticide in groundwater across Europe. The same pattern could be seen in more recent literature from European countries

---

[1] Half life time of a pesticide is the time, in days, needed for half of the amount of pesticide to be degraded (Gustafsson, 1989).

on this issue (most of them published the last five years). The most frequently found pesticide was ATZ. Based on these findings, the following research questions were formulated:

- In what kind of aquifers and geological settings are Atrazine found within Europe? In what concentrations is it found?
- Which processes in the ground do scholars identify as contributing factors for the spreading and persistency of Atrazine in the groundwater environment?
- What types of aquifers seem to be most vulnerable for the occurrence of Atrazine in groundwater?

2. Materials and Methods

This literature review on the occurrence of Atrazine in European groundwaters is mainly based on an extensive network of peer reviewed scholarly articles. The paper is based on recent studies, published during the last 5 years. However, a few older investigations and from countries outside EU have been included to cover a larger part of the intense agricultural areas in Europe. Primarily the databases 'Web of Science' and 'Scopus' and occasionally 'Google Scholar' have been used for sources. A varying combination of keywords have been used such as: *Pesticides in groundwater, occurrence of pesticides in groundwater, pesticides in European groundwater, pesticides and aquifers* as well as *Atrazine in groundwater, Atrazine in aquifers.* Relevant cited and citing references from the found literature have also been used.

The literature review has been preceded in two steps. Reading an extensive amount of literature has led to the conclusion that ATZ was one of the most frequently found pesticides in European groundwater, despite its ban in 2004 (earlier in some countries). The second part was devoted to evaluate why it is like this and what processes that might be important for the spreading of ATZ.

3. Results

3.1 Different kinds of aquifers and the occurrence of Atrazine

As shown in table 1 the investigations are conducted in aquifers with different characters. There are aquifers in unconsolidated sediments and aquifers in sedimentary rocks but there is an absence of aquifers in crystalline bedrocks. The lack of crystalline bedrock represented is due to the fact that none of the found investigation fitted the research questions or they were to old to be included in this paper. The aquifers represented in table 1 are characterized by both primary and/or secondary porosity. Primary porosity is the original porosity that is formed at the time when, for example, sediment is deposited. The secondary porosity on the other hand is formed after the deposition. It can for example be fractures or cavities caused by weathering of the bedrocks (Fetter, 2001). Out of 19 investigated aquifers 11 are conducted in some kind of sedimentary rocks and 6 of unconsolidated sediments and 3 are not specified. Eleven of the included investigations found ATZ in concentrations exceeding the EU drinking water threshold value of 0.1 μg L^{-1}.

Table 1: A study of the investigations in this literature review. Maximum concentrations of Atrazine (µg L^{-1}) are given for all investigations except for Åkesson et al. (2014) where median concentration are given. McManus et al. (2014) and Schipper and Visser (2008) only mentioned if the compound was detected or not.

Max conc µg L^{-1} ATZ	Detection frequency ATZ (%)	Hydrogeology	Degree of concealment	Location	Author
1,53	36,5	Unconsolidated, alluvial	Unconfined	Ribatejo, Portugal	Silva et al. (2012)
0,756	Most frequently	Unconsolidated, mostly alluvial	Not specified	Catalonia, Spain	Köck-Schulmeyer et al. (2014)
0,4		Consolidated, Sandstone	Confined and Unconfined	Luxembourg City	Farlin et al. (2013)
0,35	19	Not specified	Not specified	France	Lopez et al. (2015)
0,29	94,6	Unconsolidated, gravel	Unconfined	Maribor, Slovenia	Koroša et al. (2016)
0,21 ± 0,06	Most frequently	Not specified	Not specified	Italy	Fava et al. (2010)
0,2	7,3	Consolidated, Chalk	Not specified	England	Lapworth et al. (2015)
0,18		Consolidated, Sandstone	Unconfined	Doncaster, UK	White et al. (2016)
0,13	47	Consolidated, Chalk	Not specified	France	Lapworth et al. (2015)
0,13		Consolidated, Fractured	Not specified	Norway	Haarstad and Ludvigsen (2007)
0,1		Unconsolidated, alluvial	Not specified	Southern France	Sassine et al. (2016)
0,086	60,7	Consolidated, Karst, fractured sandstone	Confined and Unconfined	Mid west Germany	Reh et al. (2013)
0,057		Consolidated Sandstone,	Confined and Unconfined	Luxembourg City	Bohn et al. (2011)
0,031		Consolidated, Karst	Not specified	Jura, Switzerland	Morash (2013)
0,008 (median conc)	9,2	Unconsolidated and/or consolidated	Unconfined	Scania, Sweden	Åkesson et al. (2014)
0,0052	99,6	Consolidated, Karst, fractured limestone	Not specified	South-west Germany	Hillebrand et al. (2014)
0,0025	Not most frequently found	Consolidated, Karst, fractured limestone	Not specified	South-west Germany	Schiperski et al. (2015)
Detected		Unconsolidated, mostly sand	Not specified	The Netherlands	Schipper and Visser (2008)
Detected	4	Consolidated, Karst	Not specified	Ireland	McManus et al. (2014)

3.1.1 Fractured carbonate aquifers

Aquifers in carbonate bedrocks can have a wide range of hydrologic characteristics. Water can move through bedding planes and fractures that can get enlarged by time and dissolution of the carbonate material through water that are weakly acid. Additionally, some carbonate aquifers have a water movement through an almost homogenous and isotropic porous medium (Fetter, 2001).

Reh et al. (2013) investigated a fractured aquifer system containing an upper and a lower aquifer of limestone and dolomite separated with an aquiclude of clay and siltstone. They found a relationship between the degree of concealment and the contamination found in

groundwater. Overall the upper aquifer was more contaminated than the lower, except for one sampling point where the lower aquifer is exposed to the surface. When it comes to the Triazines, these were found in both the upper and lower aquifer while the other pesticides were only found in the upper aquifer. The scholars interpreted this result as a connection between the two aquifers, and that ATZ is persistent in the aquifer environment. ATZ was banned in Germany 1992 and therefore the scholars suggest that residence time and the vertical transport to the lower aquifers must be several years.

Lapworth et al. (2015) also found the degree of concealment and the depth of the wells to be of importance for the found concentrations. The study was performed in a large chalk aquifer of NW Europe. They found higher concentrations of ATZ where the chalk aquifer was exposed to the surface, but in contrast to Reh et al. (2013) they found lower concentrations of ATZ in the part of the aquifer with higher concealment. The scholars also suggest that rapid pathways within the aquifer can be an explanation of their findings. The aquifer is an important drinking water resource for southern England and northern France as well as parts of the Netherlands, Belgium, Germany and Denmark. This aquifer underlies Paris and London metropolitan areas as well as large agricultural areas. They agree with Reh et al. (2013) that the degree of concealment is important for the spreading of contaminants in the aquifer, although the complexity of this aquifer makes it hard to predict how the contaminants will move in the subsurface. The processes taking place in the unsaturated zone and the properties of the pesticides itself is also of importance for the findings within the aquifer. Furthermore they found similar results as Reh et al. (2013) in terms of sampling depth and the concentration of pesticides. In general, the shallower groundwater, the higher concentrations found. Lapworth et al. (2015) points out another possible explanation for the findings of ATZ in groundwater. They refer to older studies by Papiernik and Spalding (1998) and Schwab et al. (2006) where they found that ATZ is very persistent under conditions with limited oxygen. However they do not conclude if this is the case in the subsurface of the investigated area.

3.1.2 Karst aquifers

A number of investigations are conducted in karst aquifers. In Europe, karstic aquifers are of importance and stands for up to 50 % of drinking water supply in some countries (Ford and Williams, 2007). Due to the characteristics of karst aquifers, with an almost barrier free and fast recharge, they are considered as vulnerable to chemical and biological contamination (Morasch 2013). Previous studies have found fissured chalk that in partially is of a karstic character to be particularly vulnerable to rapid migration of contaminants through fissures and fractures within the aquifer (Johnson et al. 2001; Lapwoth and Gooddy, 2006; Katz et al. 2009. The complexity of the interaction between the developed karst conduits and the porous medium that serves both rapid flow and slow matrix flow and fast and long resident times respectively makes karst systems difficult to study (Hillebrand et al. 2014).

In Switzerland, Morasch (2013) investigated a karst aquifer where runoff from an agriculturally dominated area enters the aquifer through a swallow hole and where the infiltrated water is diluted with deep groundwater and reappears in two springs that discharge the aquifer. Morasch (2013) sampled both water from the swallow hole and from the springs and found different behavior of the investigated pesticides. In May pulses of higher concentrations of ATZ in the swallow hole were observed and explained with recently applied pesticides in the area. Different behavior was observed in the springs, the corresponding pulse of higher concentrations in the springs could be observed for other pesticides, while concentrations ATZ remained constant in the springs. The scholar suggests that ATZ has been attached to interakarstic matrix and that the washout created the stable concentration of ATZ in the springs. The pulse of higher concentrations could be explained by the lack of intense rainfall during the sampling campaign, leading to the conclusion that there are differences in the behavior of the pesticides that resulted in differences in

concentrations in the springs. Hillebrand et al. (2014) concluded the same behavior for ATZ in a karst aquifer in southwest Germany. ATZ is considered to be located within the aquifer material and it is released slowly to the groundwater. The differences between these two investigations are that ATZ has been banned in Germany 1992 and in Switzerland it is still in use (at the time of the sampling). Hillebrand et al. (2014) state that the concentrations of ATZ are likely related to long residence time due to slow groundwater flow inside the karst matrix in combination with low, or no degradation. They further state that the application of ATZ must also be considered. The amount of applied ATZ is reflected in the amounts found in the groundwater. Another study in the same aquifer in southwest Germany by Schiperski et al. (2015) was investigating the relationship between organic micorpollutants and hydro-sedimentary processes in groundwater before and after a heavy rain event. They measured the concentrations of ATZ in spring water discharging the aquifer. They are in agreement with the findings of Hillebrand et al. (2014), namely that ATZ is probably located within the matrix of the aquifer. Schiperski et al. (2015) found a higher concentration of ATZ in the discharging spring water before the rain event and a lower concentration after and this would, according to the scholars, be a result of dilution from freshly infiltrated water to the aquifer. During the flush of the aquifer system the concentration of ATZ remained rather constant, while turbidity increased slightly. The scholars argue that the increase in turbidity is an indication of resuspension of previously deposited particles suggesting that ATZ is located within the aquifers matrix.

3.1.3 Sandstone aquifers

Sandstone aquifers can, due to its sedimentary origin have both primary and secondary porosity and build up complex groundwater systems. Two investigations have been conducted in the same area by Farlin et al. (2013) and Bohn et al. (2011). This is a complex system of a fractured sandstone aquifer that is partly confined and partly unconfined and an important drinking water supply on a regional scale in Luxembourg. The physical and geochemical properties are heterogeneous with dense and hard sandstone altered by parts of brittle limestone (Farlin et al. 2013). Colbach (2005) determined the porosity of the aquifer and concluded that the primary porosity ranged from 5 to 40 % depending on the degree of dissolution of the calcareous matrix. Secondary porosity was estimated to approximately 1 % and he further concluded that parts of the aquifer transmit water in ways that is comparable to a karstic formation. The aquifer is mainly covered by well-drained sandy soils that make the groundwater potentially vulnerable to agricultural pollution due to its high hydraulic conductivity. The study design of Bohn et al. (2011) was to investigate the occurrence of ATZ and its degradation products in the drinking water in Luxemburg where they found ATZ, DEA and DIA in both spring water and tap water. They state that even though the compound has been banned for a relatively long time (since 2004 in Luxembourg) it is still detectable in groundwater. Farlin et al. (2013) sought to study the transport time for pesticides through the soils and in the aquifer. They concluded that the relatively higher concentrations found in some of the springs was due to the sandy soil in the recharge area connected to these springs. They point out that sandy soil has a higher hydraulic conductivity, which facilitates the transport of pesticides through the subsurface. The pesticides are therefore flushed out of the biological active soil zone and have therefore less time to degrade. Hence, a higher concentration of the pesticide is found in the groundwater. However where there are fractures with greater flow, this can dilute the concentrations of pesticides found in groundwater. The same patterns were found by White et al. (2016) that studied unconfined sandstone aquifer in Doncaster, UK. White et al. (2016) could see a relationship between the detected ATZ concentrations and the conductivity through the aquifer. Where there were higher flow rates the concentrations were lower due to an effect of dilution and higher concentrations were found in parts of the aquifer where flow rates are slower and residence time longer. For the behavior of ATZ and metabolites in the subsurface Farlin et al. (2013) and White et al. (2016)

state that the spreading and occurrence of this pesticide in the groundwater environment is a result of a complex combination factors including; the amount of ATZ applied on the fields in the recharge area, the physical properties of the compound itself, the soil moisture, depth of the unsaturated zone, the hydraulic conductivity and chemical properties of the soil and the nature of the groundwater flow within the aquifer. Furthermore, Bohn et al. (2011) explains the detection of ATZ and metabolites in tap and spring water with the long persistency of the compound in the environment and refers to Krutz et al. (2010) that concluded that the half-life time of the compound is considered to be 28-178 days in deeper soil layers or water.

3.2.4 Aquifers in unconsolidated sediments with hydraulic connection to surface water

Three investigations are done in aquifers of unconsolidated sediments with a hydraulic connection to surface water. An aquifer can be hydraulic connected both in terms of losing or gaining water from the surface water. This can differ, a stream or surface water can be both losing and gaining in different parts, or it can change seasonally (Fetter, 2001). All investigations are done in aquifers of a highly permeable material of sand or gravel. These materials have a high hydraulic conductivity, which means that water moves fast through the material. Koroša et al. (2016) evaluated the contamination of micro pollutants in an intergranular aquifer in Maribor, Slovenia. This aquifer is recharged from precipitation, the Drava River and infiltration and therefore considered as vulnerable to surface-derived contaminants. They found the river to have a dilution effect on the concentrations found in groundwater. The sampling points with connections to the surface water were found with lower concentrations than sampling points where recharge is mainly from local precipitation. ATZ was found in high concentrations (0,29 µg L^{-1}) in groundwater and Koroša et al. (2016) suggest a few possible explanations for the findings of ATZ in the samples. It can be due to the persistency of ATZ in the environment, or a long time lag in the soil profile or possibly an illegal use of ATZ after its ban. The scholars used a calculation of the ratio between ATZ and DEA, the DAR ratio (developed by Adams and Thurman, 1991). Through this ratio a determination of the freshness of the ATZ contamination can be made. The ratio between DEA/ATZ were a low ratio is representing more ATZ in relation to DEA in the groundwater and is therefore an indication of a freshly applied ATZ with short residence time (i.e shorter time to degrade). In general they found higher concentrations of the metabolites than ATZ in the samples and therefore Koroša et al. (2016) suggests that the concentrations of ATZ found are deriving from non-point sources in the area and that the likelihood of illegal use is low. They further mention that ATZ and its metabolites are known to be persistent. Previous studies have found that they can form strong chemical bounds with organic carbon and clay in sediment. Where there are sediments with a low content of these particles these compounds can move through the subsurface and contaminate the groundwater (Aelion and Marthur, 2001). However, Koroša et al. (2016) do not mention the clay or organic content in the investigated sediment.

Another study was performed in the Ribatejo region in Portugal by Silva et al. (2012). The aquifer is located in alluvial deposits where the Tagus River and tributaries strongly influences the groundwater flow in the aquifer and are both recharging and discharging the aquifer depending on the hydraulic potential. Intensive agriculture is dominating the area and the study was performed in 2004 and 2005 i.e. ATZ was still in use. Silva et al. (2012) do not mention the influence of the river despite the fact that all wells except of two are located right in the bank of the Tagus River. However they could conclude a correlation between detections of pesticides and the sampling period. In general more pesticides found during spring and autumn. For ATZ slightly higher concentrations was detected during the spring and autumn. The scholars explain these findings with the location of the water table. In spring the water table is located closer to the surface due to the end of a wet period. Whereas during the autumn, recent harvesting and the beginning of a wet period increase the likelihood of pesticides leaching to groundwater. Furthermore they concluded that the

movement through the soil matrix is rather rapid. They calculated the DAR ratio and interpreted the low ratios as rapid movement of ATZ to the groundwater. Silva et al. (2012) further found a combination of pesticide occurring together in many of the samples. These pesticides (alachlor, ATZ, ethofumesate, metolachlor, metribuzin and DEA) have similar leaching potential and are considered as *leachers* or *transitions* according to GUS index[2]. Silva et al. (2012) state that this points out the importance of the leaching potential of the component in combination with the permeability of the soil matrix. They further state that the aquifer is vulnerable to surface-derived contamination due to the higher permeability of the matrix and the intensive agriculture in the area. They point out the importance of the river for the recharge and the discharge of the aquifer, however they do not mention this in the results.

The third reviewed study in this section is by Sassine et al. (2016) and the study is performed in a shallow alluvial aquifer in southern France. It has a hydraulic conductivity (K) between 3 · 10⁻³ to 10 · 10⁻⁴ m s⁻¹, a medium permeable material. It is locally influenced by surface water, and from imported water from Rhône River that is used for artificial groundwater recharge and irrigation. The main recharge is by precipitation and lateral flow from a karst aquifer in the vicinity. The studied aquifer is mainly covered by agriculture and has a relatively thin unsaturated zone of about 2-7 m that makes this aquifer vulnerable for pesticide contamination. The recharge from the karst aquifer is considered as less affected by pesticide contamination due to its coverage of scrublands. A Quaternary fluvial silt deposit with a low permeability overlies one part of the aquifer. Samples were collected from the karst aquifer and the surface water for comparison. The groundwater samples from the karst aquifers showed lower concentrations than those in the alluvial aquifer. Sassine et al. (2016) argue that this is probably related with the land use as the karst aquifer is covered with scrublands. The sampled surface water contained very low concentration of triazines and in agreement with the findings of Koroša et al. (2016); the surface water is thought to be an important factor in the dilution of the concentrations in the groundwater. The sampling also showed that the concentrations are lower where the aquifer is recharged by the karst aquifer, a result of dilution with less contaminated water. The highest concentrations were found in groundwater in the part of the aquifer that is covered by a layer of lower permeable silt deposits. According to the scholars this layer may have hindered recharge by infiltration and therefore also the dilution of the pesticides. Hence, they conclude that the concentrations of the pesticides are not only a result of the application but that it is also influenced by the origin of the recharge water to the groundwater. They further investigated the relation between concentrations of triazines in relation to depth and could identify three general trends. Firstly, where the aquifer is recharged by stream water or lateral recharge from neighboring aquifers, the concentration rates of triazines were similar throughout the depth. Secondly, the scholars argue that when higher concentrations are found in deeper parts this could be a result of dilution from recent infiltrated water that does not contain much ATZ due to its ban several years ago. The third trend is high concentrations of triazines in the shallow parts of the aquifer and the researchers state that this can have two possible explanations. Firstly, a slow remobilization or washout rate of the triazines because they are persisting in the unsaturated zone due to the processes that could affect these compounds such as pH, organic carbon and/or clay content. The second hypothesis is a recent illegal use of these pesticides. However, when Sassine et al. (2016) compared their results to monitoring results (SMNVC, 2002) in the same aquifer they could state that the concentrations have decreased and therefore, the scholars state that the first hypothesis is more likely than illegal use. When the scholars compared the age of the groundwater to the concentrations of ATZ they could conclude that older groundwater contained higher concentrations of ATZ, which is in

---

[2] The groundwater ubiquity score (GUS index) can be used to estimate the potential of pesticides to contaminate groundwater. To obtain the GUS index the calculations include the persistence of pesticides, the binding ability of pesticides to soil particles with the following equation: $GUS = \log_{10}(\frac{1}{2} \text{ life time})(4\log_{10}(Koc))$ (Gustafsson, 1989).

agreement with the fact that ATZ is banned and older groundwater would for that reason contain more ATZ.

3.2 Surveys conducted on a national or regional scale.

In general, the study designs of the following surveys are to determine the occurrence of pesticides in groundwater on a regional or national wide scale. The scholars have evaluated the current contamination status in groundwater with an overall focus on agricultural areas. The aims are to mainly provide information about the amount of pesticides found, their concentrations and (for some investigations) what kind of aquifers that seems most vulnerable to pesticide contamination. It is important to note that all studies are not only focusing on ATZ, they include a large group of different micro pollutants with anthropogenic origin.

Several of the investigations included in this section have focused on what kind of geological setting are found to be the most vulnerable to pesticide contamination. Important to note here is that these investigations have found what seems to be the most vulnerable aquifer of the aquifers included in their surveys. McManus et al. (2014) investigated aquifers throughout Ireland and focused on what kind of physical characteristics of the geological setting that were most associated with the detection of pesticides in groundwater. Through statistical analyses they found aquifers with a high transmissivity[3] as in karstic flow, fissured flow as well as intergranular flow regime aquifers to be the most vulnerable aquifers to pesticide contamination. Moreover they could conclude that karst aquifers overlain by alkaline Quaternary deposits were vulnerable. McManus et al. (2014) suggest that in an aquifer with low transmissivity, there are less movement of particulate material and therefore longer contact time with absorbent material which leads to that more attenuation mechanism can take place. When it comes to fractures they state that these can act as fluid pathways allowing more movement of pesticides within the aquifer. Moreover they state that fractured bedrocks in combination with a thin soil cover were more associated with pesticide detections throughout Ireland. This is in line with the research of Haarstad and Ludvigsen (2007) in Norway. The fractured bedrock aquifers had the most detection of pesticides. However, the differences between these two investigations is that Haarstad and Ludvigsen focused on agricultural areas while McManus et al. (2014) tried to cover a variation of hydrogeology and pressures on groundwater. McManus et al. therefore include study areas where the contamination of pesticides is not significant while Haarstad and Ludvigsen only focus on areas where the contamination of pesticides is already known to be an issue. Another study that covered a wide arrange of geological settings is one by Åkesson et al. (2014) that investigated the occurrence of pesticide in Scanian groundwater in Sweden. The geology of Scania spans from Precambrian crystalline bedrocks, sedimentary bedrocks and Quaternary deposits, thus a variation of aquifers were included in the study. In Sweden, ATZ have been prohibited since 1989 and this is also one of the investigations that found the lowest concentrations of ATZ in groundwater (and for this study only median concentrations are given). Åkesson et al. (2014) found groundwater tapped from shallow filters in unconfined aquifers with primary or secondary porosity with modern and oxic-suboxic waters to be the most contaminated types of groundwater. Moreover, they stated that pesticides were often found together which is in line with what Silva et al. (2012) stated. Schipper et al. (2008) conducted an investigation in 9 out of 12 provinces in the Netherlands. They focused on the relationship between depth and the occurrence of pesticides in groundwater and found that pesticides were found in similar concentration ranges regardless of depth. Most of the groundwater samples were taken in aquifers of unconsolidated sand

---

[3] Transmissivity: A rate at which water with a certain viscosity and density is transmitted through a unit of a porous media i.e a function of the properties of the water, the porous media and the thickness of the porous media (Fetter, 2001).

and they could conclude that the attenuation processes in the upper part of the soil cannot prevent the leaching of pesticides to deeper groundwater.

An additional three studies of national or regional wide determination of pesticides in groundwater have been conducted with no focus on the geological setting. One of the identified controlling factors of the fate of pesticides in groundwater is land use, as stated by Lopez et al. (2015) as well as Åkesson et al. (2014). Both these studies found more pesticides in higher concentrations in the sampling points that were influenced by both agriculture and urban land use. Fava et al. (2010) found the relationship between land use in the choice of cultivated crops and found pesticides. ATZ is mainly used for maize and in the areas where maize is produced, the highest concentrations of ATZ are found. Fava et al. (2010) further state that other important factors controlling the leaching of the pesticides is the nature of the soil and the amount of pesticides applied on the fields as well as the characteristics of the pesticide itself. The pesticides that are most commonly found are often also correlated with their tendency to leach. ATZ is according to the GUS index classified as a leacher (IUPAC, 2016). This is pointed out by Silva et al. (2012), Åkesson et al. (2014) and Köck-Schulmeyer et al. (2014) (a study conducted in Catalonia, Spain) as an important factor in the occurrence of pesticides in groundwater. They also concluded that many pesticides with high leachability are often found together.

Köck-Schulmeyer et al. (2014) argue that the use of irrigation is an indirect factor controlling the pesticides in groundwater. The more irrigation, the more cultivation is possible and with more cultivation, more pesticides are applied on the fields leading higher concentrations of pesticides found in groundwater. In addition, a lot of areas in Catalonia also reuse treated wastewater (Bixio et al. 2006) and previous studies from Catalonia showed high levels of pesticides in the wastewater treatment plants effluents (Köck-Shulmeyer et al. 2013). This is also confirmed by the fact that the most contaminated areas of the investigation is located in areas where they use most irrigation.

3.3 Atrazine in the receiving environment

In the studied literature about ATZ there are a few factors pointed out as important for the environmental fate of the compound. For the scope of this literature review the highlighted factors will be shortly described but not further reviewed.

Adsorption to organic matter and clay minerals in the soils has been highlighted as an important factor controlling the transport of ATZ towards the groundwater (McManus et al. 2014; Koroša et al. 2016; Sassine et al. 2016). ATZ and its metabolites are known to be persistent. The role of adsorption to organic matter and/or clay is that it should retard ATZ in its transport towards the groundwater (Aelion and Marthur 2001; Inoue et al. 2004; Mudhoo and Garg, 2010: Park et al. 2003). K_d (the distribution coefficient) has been used to determine how apt herbicides are to move to a solid or liquid phase. K_d is the ratio between the equilibrium concentrations of an absorbed substance on a solid sorbent and the dissolved in the liquid phase (Ebato et al. 2002). A further calculation using K_d in combination with the organic content of the soil i.e. the product of K_d and the organic content of the soil (mass) give K_{oc} (Ecotec, 2016). Kultikova and Perminova (2002) found K_{oc} values for ATZ ranging from around 100 to 570 L kg^{-1}C of soil humic acids and soil fluvic acids respectively. They further state the fate and transport of ATZ in the soil is highly dependent on what kind of organic material that is found in the ground. Regarding the amount of organic content, Ebato et al. (2002) studied forty soil samples whereof many had been cultivated and also found the amount of organic content in the soil to be the dominant factor controlling the adsorption of ATZ. Interestingly they also found that when more ATZ was applied on the samples, a smaller percentage of it was adsorbed and the researchers explain this with the adsorptive sites in the soil decreases with increasing application.

ATZ is an uncharged pesticide and Clausen et al. (2001) found, when comparing the absorption to kaolinite, calcite, quartz and α-alumnia that ATZ only adsorb to kaolinite at pH around 6. Quartz could adsorb ATZ to a minor extent when the pH was lowered to 2,4 but showed no significant adsorption at pH 6. However pH can have an effect on the adsorption Sassine et al. 2016 also mention the importance of the pH in the receiving environment. According to Saint-Fort (1988) pH in the medium has an indirect effect on the adsorbent ATZ adsorption by both clay minerals and organic matter increases when the pH of the solution decreases.

ATZ and its main metabolites mentioned in this literature review, DIA and DEA behave slightly different in the environment. Studies indicate that the most common mechanism of microbial degradation is dealkylation (Aelion and Mathur, 2001) where some microorganisms remove the isopropyl group in the forming of DIA and the ethyl side group in the forming of DEA (Ericksson, 1989). DIA and DEA are more soluble in water than Atrazine (670 mg L^{-1} 3200 mg L^{-1} respectively, 33 mg L^{-1} for ATZ) and can therefore have a greater potential to contaminate groundwater than ATZ (Aelion and Mathur, 2001). Furthermore the degradation in groundwater is slower due to lower bacterial occurrences. However, it should also be noted that DEA could degrade from both ATZ and another triazine, propazine although it is less frequently used in Europe. DIA can also be a degradation product from simazine, cyanazine and ATZ (Scribner et al. 2005).

4. Discussion

The included investigations are conducted in karst-, sedimentary bedrock- and unconsolidated aquifers. Some of the aquifers are chosen due to known pesticide contamination and they are all located in areas of agriculture of a more or less intense nature. One can also speculate, that this kind of aquifers are located within areas of agriculture due to the fertile soil they often are surrounded with. The included unconsolidated aquifers are often of alluvial origin and this is also often associated with fertile soil. This could also be a reason why no study was conducted in a crystalline bedrock aquifer, because they are not always located in geological settings that give fertile soils. Important to note is also that if the scope of the investigations was to determine the occurrence of pesticides in groundwater, it is logical that the focus has been in areas of agriculture.

When taking the found concentrations into consideration, the karst aquifers seem to be least contaminated with ATZ. However the found concentrations can also be due to the theory by Morasch (2013) and Hillebrand et al. (2014) that ATZ is attached to the intrakarstic matrix, and therefore found in lower concentrations. Moreover, the fractures and fissures in aquifers can lead to higher flow rates and therefore contribute to dilution of the contaminated groundwater. If the movement of water is taking place in both fractures and pores, as stated by Hillebrand et al. (2014) this types of aquifers can be difficult to study due to the complexity. The investigations that found the highest concentrations were both located in alluvial aquifers in areas with intensive agriculture. The permeability of the soil can play a role here, that pesticides are moving easily through the soil column towards the groundwater and may not contain a significant amount of organic matter or clay particles that can retard the movement of ATZ. However it has been hard to determine the movement through the soil column because none of the included investigations have included the unsaturated zone and the matrix therein and therefore conclusions regarding that are hard to make. Noteworthy regarding the study made by Silva et al. (2012) (who found the highest concentration of ATZ) is that while ATZ was still in use for the time of the sampling, he concentrations might be higher than in many of the other investigations where ATZ have not been used for at several years and ATZ have had time to degrade in the subsurface.

The degree of concealment has showed two trends. Reh et al. (2015) found higher concentrations of ATZ in areas with lower concealment in the aquifer while Lapworth et al. (2015) and Sassine et al. (2016) found higher concentrations in areas with higher degree of concealment. This seems to be a result of several factors. When there is no concealment of the aquifer the contaminants can move faster to the groundwater. On the other hand, when the aquifer is covered with a layer with a low hydraulic conductivity, this could retard the movement of contaminants but it can also hinder dilution of groundwater. Hence it can lead to both lower concentrations as the movement of contaminants is retarded. However, the contaminants that do reach the aquifer can be found in higher concentrations due to lack of dilution.

Regarding the national or regional wide studies, the design of these investigations, are including the geological settings that exist in that country or region. The most vulnerable setting found in one region does not have to be the same in the next region due to: the differences in geological setting, amount of pesticides applied and the controlling factors in the receiving environment and that every environment in this sense is unique and the controlling factors are differ from one setting to another.

The spreading and fate of ATZ in the environment is a complex combination of factors and the information in the investigations included in this literature review have not always provided information about what the scholars have stated as controlling factors. This is the case since none of the investigations had the aim to explore why ATZ was found in the groundwater. Instead they had a screening nature with the purpose to investigate weather an aquifer was contaminated or not. As mentioned in the beginning of this section, studies have also chosen areas that are known to be contaminated, intense agricultural areas and screening for micro-pollutants that are known to be persistent. This can be interpreted as a bias in the sense that this does not show a clear picture of the situation throughout Europe. However intensive agriculture seem to contaminate the groundwater regardless of aquifer type and the contamination rate and extent seem to have more to do with the chemical properties of the pesticide and the processes in the unsaturated zone.

In conclusion, the highlighted factors controlling the fate of ATZ are the characteristics of ATZ itself, the matrix in the unsaturated zone and the ability it has to absorb the compound and the nature of the aquifer itself and this in combination with the overlaying soil, the degree of concealment and the land use in the recharge area. One should keep in mind that ATZ is known to be persistent in the environment and therefore it is also found in the environment even if the last application was decades ago. It has been banned in the European Union for this reason, and the EU is doing a lot in the work towards good ecological and chemical status in this vulnerable natural resource that groundwater is. However a lot more work has to be done as not everything is well understood about the fate of contaminants in the environment. The growing population and in the same rate, growing demand of food supplies the use of pesticides is not likely to end but careful use and further research is needed to find compounds that are affecting the environment and ecosystems as little as possible.

5. Literature

Adams, Craig, D. and Thurman, Earl, Michael. 1991. Formation and transport of deethylatrazine in the soil and vadose zone. *Journal of Environmental Quality* 30:540-547.

Aelion, C., Marjorie and Mathur, P., Priti. 2001. Atrazine biodegradation to deisopropylatrazine and deethylatrazine in coastal sediments of different land uses. *Environmental Toxicology and Chemistry* 20:2411-2419.

Bixio, D, Thoeye, D, De Koning, J, Joksimovic, D, Savic, D, Wintgens, T, Melin, T. 2006. Wastewater reuse in Europe. *Desalination* 187:89-101.

Bohn, Torsten, Cocco, Emmanuelle, Gourdol, Laurent, Guignard, Cédric, Hoffmann, Lucien. 2011. Determination of atrazine and degradation products in Luxembourgish drinking water: origin and fate of potential endocrine-disrupting pesticides. *Food Additives and Contaminants* 28:1041-1054.

Clausen, Worsøe, Lotte, Fabricius, Ida, Lykke, Madsen, Lene. 2001. Adsorption of Pesticides onto Quartz, Calcite, Kaolinite, and α-Alumina. *Journal of Environmental Quality*. 30:846-857.

Colbach, Robert. 2005. Overview of the geology of the Luxembourg sandstone(s). *Ferrantia* 44:155-160.

Donati, Loredana, Funari, Enzo. 1993. Review of leaching characteristics of triazines and their degradation products. *Annali dell'Instituto Superiore di Sanità* 29(2):225-241.

Ebato, Munehiro, Matsumura, Kenichi, Yonebayashi, Koyo. 2002. Effects on soil characteristics on Atrazine and Linuron adsorption. *Journal of Pesticide Science* 27:337-346.

Ecotec. 2016. European center for ecotoxicology and toxicology of chemicals. *Technical report 123 Definition.* http://www.ecetoc.org/report/measured-partitioning-property-data/adsorption-desorption-distribution-kd-and-organic-carbon-water-partition-koc-coefficients/koc-definition/
(Recived: 2016-12-11)

Ericksson, Larry, Eugene. 1989. Degradation of atrazine and related s-triazines. *Critical Reviews in Environmental Control.* 19(1):1-14.

European Commision, Environment, 2016. *History of groundwater EU legislative development.* 2016-06-08. http://ec.europa.eu/environment/water/water-framework/groundwater/history.htm (Received: 2016-11-14)

European Commision Decision of 10 March 2004 concerning the noninclusion of atrazine in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisation for plant protection products containing this active substance (notified under document number C(2004)731) (2004/248/EC)

European Parliament and of the Council Directive 2000/60/EC of the 23 October 2000 establishing a framework for Community action in the field of water policy.

European Parliament and of the Council Directive 2006/118/EC of 12 December 2006 on the protection of groundwater against pollution and deterioration.

European Parliament and of the Council Directive 2008/105/EC of the 16 December 2008 on the environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC

Farlin, Julien, Drounet, L, Gallé, Tom, Pittos, D, Bayerle, Michael, Braun, Christian, Maloszewski, Piotr, Jan, Vanderborght, Jan, Elsener, Martin, Kies, Antoine. 2013. Delineating spring recharge areas in a fractured sandstone aquifer (Luxembourg) based on pesticide mass balance. *Hydrogeology Journal* 21:799-812.

Fava, Luca, Orrù, Antionietta, Maria, Scardala, Simona, Alonzo, Elena, Fardella, Maristella, Strumia, Caterina, Martinelli, Angiolo, Finocchiaro, Sabrina, Previtera, Massimo, Franchi, Alessandro, Calà, Pergiuseppe, Dovis, Mauro, Bartoli, Donatella, Sartori, Guiseppe, Broglia, Lia, Funari, Enzo. 2010. Pesticides and their metabolites in selected

Italian groundwater and surface water used for drinking. *Annali dell'Instituto Superiore di Sanità* 46(3):309-316

Fetter, Charles, Willard. 2001. *Applied hydrogeology*. 4th edition. Upper Saddle River: Prentice Hall.

Ford, Derek, Williams, Paul, D. 2007. *Karst Hydrogeology and Geomorphology*. New York. Wiley

Graymore, Michelle, Stagnitti, Frank, Allinson, Graeme. 2001. Impacts of atrazine in aquatic ecosystems. *Environment International* 26:483-495.

Gustafson, David, I. 1989. Groundwater Ubiquity Score: a simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry* 8(4):339-357.

Haarstad, Ketil and Ludvigsen, Gro, Hege. 2007. Ten Years of Pesticide Monitoring in Norwegian Ground Water. *Ground Water Monitoring & Remediation* 27(3):75-89.

Hillebrand, Olav, Nödler, Karsten, Geyer, Tobias, Licha, Tobias. 2014. Investigating the dynamics of two herbicides at a karst system in Germany: Consequences for sustainable raw water management. *Science of the Total Environment* 482-483:193-200.

Inoue, Miriamhioko, Oliveira, Ruben, Silvéro, Regitano, Jussara, Borges, Tormena, Cássio, Antonio, Constantin, Jamil, Tornisielo, Valdemar, Luiz. 2004. Sorption kinetics of atrazine and diuron in soils from southern Brazil. *Journal of Environmental Science and Health*. 39:589-601.

IUPAC, International Union of Pure and Applied Chemistry. 2016. *Atrazine (Ref: 30027)* 2016-01-13. http://sitem.herts.ac.uk/aeru/iupac/Reports/43.htm#none (Received: 2016-12-10)

Johnson, Andrew, C., Belsien, Tim, J., Bhardwaj, C, Lal., Dixon, Andy, J., Gooddy, Daren, C., Haria, Atul, H., White, Craig, M. 2001. Penetration of herbicides to groundwater in an unconfined chalk aquifer following normal soil application. *Journal of Contaminant Hydrology*. 53:101-117.

Katz, Brian, G., Griffin, Dale, Warren, Davis, Jason, Hal. 2009. Groundwater quality impacts from the land application of treated municipal wastewater in a large karstic spring basin: chemical and microbiological indicators. *Science of the Total Environment* 407:2872-2886.

Koroša, Anja, Auersperger, Primož, Mali, Nina. 2016. Determination of micro-organic contaminants in groundwater (Maribor, Slovenia). *Science of the Total Environment* 571:1419-1431.

Krutz, L., Jason, Shaner, Dale, L., Weaver, Mark, A., Webb, Richard, M., T., Zablotowicz, Robert, M., Reddy, Krishna, N., Huang, Yanbo, Thomson, Steven, James. 2010. Agronomic and environmental implications of enhanced s-triazine degradation. *Pest Management Science* 66:461-481.

Kucka, Marek, Pogrmic-Majkic, Kristina, Fa, Svetlana, Stojilković, Stanko, S., Kovačević, Radmila, Ž., 2012. Atrazine acts as an endocrine disrupter by inhibiting cAMP-specific phoshodiesterase-4. *Toxicology and Applied Pharmacology* 265:19-26.

Kultikova Natalia and Perminova Irina. 2002. Binding of Atrazine to Humic Substances from Soil, Peat, and Coal Related to Their Structure. *Environmental Science and Technology*. 36:3720-3724.

Köck-Schulmeyer, Marianne, Villagrasa, Marta, López de Alda, Miren, Céspedes-Sánchez, Raquel, Ventura, Francesc, Barceló, Damià. 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. *Science of the Total Environment* 458-460:466-476.

Köck-Schulmeyer, Marianne, Ginebreda, Antoni, Postigo, Cristina, Garrido, Teresa, Fraile, Josep, Lópes de Alda, Miren, Barceló, Damirà. 2014. Four-year advanced monitoring program of polar pesticides in groundwater of Catalonia (NE-Spain) *Science of the Total Environment* 470-471:1087-1098.

Lapworth, Dan, J. and Gooddy, Daren, C. 2006. Source and persistence of pesticides in a semiconfined chalk aquifer of southeast England. *Environmental Pollution*: 144:1031-1044.

Lapworth, Dan, J, Baran, Nicole, Stuart, Marianne, E, Manamsa, Katya, Talbot, Julie, C. 2015. Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. *Environmental Pollution* 203:214-225.

Loos, Robert, Locoro, Giovanni, Comero, Sara, Contini, Serafino, Schwesig, David, Werres, Friedrich, Balsaa, Peter, Gans, Oliver, Weiss, Stefan, Blaha, Ludek, Bolchi, Monica, Gawlic, Manfred, Bernd. 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Research* 44:4115-4126.

Lopez, Benjamin, Ollivier, Patrick, Togola, Anne, Baran, Nicole, Ghestem, Jean-Phillipe. 2015. Screening of French groundwater for regulated and emerging contaminants. *Science of the Total Environment* 518-519:562-573.

McManus, Sarah-Louse, Richards, Karl, G., Grant, Jim, Mannix, Anthony, Coxon, Catherine, E. 2014. Pesticide occurrence in groundwater and the physical characteristics in association with these detections in Ireland. *Environmental Monitoring and Assessment* 186:7819-7836.

Morasch, Barbara. 2013. Occurrence and dynamics of micropollutants in karst aquifer. *Environmental Pollution* 173:133-137.

Mudhoo, Ackmez and Garg, Vinod, Kumar. 2010. Sorption, Transport and Transformation of Atrazine in Soils, Minerals and Composts: A Review. *Pedosphere* 21(1):11-25.

Papiernik, Sharon, K., Spalding, Roy, F. 1998. Atrazine, Deethylatrazine, and Deisopropylatrazine Persistence Measured in Groundwater in Situ under Low-Oxygen Conditions. *Journal of Agriculture and Food Chemistry* 46(2):749-754.

Park, Jeonghun, Feng, Yucheng, Ji, Pingsheng, Voice, Thomas, C., Boyd, Stephen, A. 2003. Assessment of bioavailability of soil-sorbed atrazine. *Applied and Environment Microbiology.* 69:3288-3298.

Radosevich, Mark, Triana, Samuel, J., Tuovinen, Olli, H. 1989. Biodegradation of atrazine in surface soils and subsurface sediments collected from an agricultural research farm. *Biodegradation* 7:137-149.

Reh, Ronald, Licha, Tobias, Geyer, Tobias, Nödler, Karsten, Sauter, Martin. 2013. Occurrence and spatial distribution of organic micro-pollutants in a complex hydrogeological karst system during low flow and high flow periods results of a two-year study. *Science of the Total Environment* 443:438-455.

Saint-Fort, Roger. 1988. Study of interactions between atrazine, diazinon, and lindane with humic acids of various molecular weights. *Journal of Environmental Science and Health.* 23(6):613-624.

Sassine, Lara, La Gal La Salle, Corinne, Khaska, Mahmoud, Verdoux, Patrick, Meffre, Patrick, Benfodda, Zohra, Roig, Benoît. 2016. Spatial distribution of triazine residues in a shallow alluvial aquifer linked to groundwater residence time. *Environmental Science and Pollution Research.* 1-11.

Schiperski, Ferry, Zirlewagen, Johannes, Hillebrand, Olaf, Nödler, Karsten, Licha, Tobias, Scheytt, Traugott. 2015. Relationship between organic micropollutants and hydro-sedimentary processes at a karst spring in south-west Germany. *Science of the Total Environment* 532:360-367.

Schipper, Peter, Visser, Mark, van der Linden, Antonius 2008. Pesticides in ground water and drinking water wells; overview of the situation in the Netherlands. *Water Science and Technology* 57(8):1277-1286.

Schocken, Mark, J., Speedie, Marilyn, K. 1984. Physiological aspects of atrazine degradation by higher marine fungi. *Archives of Environmental Contamination and Toxicology* 13:707-714.

Schwab, Arthur, Paul, Splichal, P. A., Banks, Margaret, Katherine. 2006. Persistence of atrazine and alachlor in ground water aquifers and soil. *Water, Air, and Soil Pollution.* 171:203-235.

Scribner, Elisabeth, A., Thurman, E., M., Goolsby, Donald, A., Meyer, Michael, T., Battaglin, William, A., Koplin, Dana, W. 2005. *Summary of significant results from studies of*

triazine herbicide and their degradation products in surface water, and precipitation in the midwestern United states during the 1990s. US Department of the Interior, US Geological, Survey. Washington DC.

Silva, Emília, Mendes, Maria, Paula, Ribeiro, Luís, Cerejeira, Maria, José. 2012. Exposure assessment of pesticides in shallow groundwater of the Tagus vulnerable zone (Portugal): a multivariate statistical approach (JCA). *Environmental Science and Pollution Research* 19: 2667-2680.

SMNVC. 2002. Suivi des pesticides. Interprétations des résultats et premières conclusions (In French).

Švorc, Ľubomír, Reivaj, Miroslav, Bustin, Dušan. 2013. Green electrochemical sensor for environmental monitoring of pesticides: Determination of atrazine in river water using a boron-doped diamond electrode. *Sensors and Actuators* 181:294-300.

White, Daniel, Lapworth, Dan, J., Stuart, Marianne, E., Williams, Peter, J. 2016. Hydrochemical profiles in urban groundwater systems: New insights into contaminant sources and pathways in the subsurface from legacy and emerging contaminants. *Science of the Total Environment.* 562:962-973.

World Health Organization. 2010. *Atrazine and Its Metabolites in Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality.* WHO/HSE/WSH/10.01/11. Geneva. WHO Document Production Services.

World Water Assessment Programme (WWAP). 2009:3 Third United Nation World Water Development Report. *Water in a changing world.* Paris, Unesco publishing.

Xing, Houjuan, Wang, Xu, Sun, Gang, Gao, Xuejiao, Xu, Shiwen, Wang, Xiaolong. 2012. Effects of atrazine and chlorpyrifos on activity and transcription of glutathione S-transferase in common carp (Cyprinus cario, L.) *Environmental Toxicology and Pharmacology.* 33:233-244.

Åkesson, Maria, Sparrenbom, J., Charlotte, Dahlqvist, Peter, Fraser, J., Stephen. 2014. On the scope and management of pesticide pollution of Swedish groundwater resources: The Scanian example. *The Royal Swedish Academy of Science.* 44:226-238.