SOCOPSE

SOURCE CONTROL OF PRIORITY SUBSTANCES IN EUROPE

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SOCOPSE
Source Control of Priority Substances in Europe

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An Inventory and Assessment of Options for Reducing Emissions: Atrazine

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An Inventory and Assessment of Options for Reducing Emissions: Atrazine

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Contents

1. Executive summary

Atrazine was widely used in the European agriculture as an herbicide. Due to its high mobility Atrazine leaked to the groundwater, surface water and drinking water wells. When Atrazine enters the environment it will breakdown quit rapidly under a wide range of normal use conditions (43 days). When Atrazine enters the groundwater it may remain there for a long time because breakdown of the chemical is very slow.

The European Commission decision 2004/248/EC not to include Atrazine on Annex I to Directive 91/414/EC specify phase out of the use in the EU. According to Article 3 all Member States except 4 could allow Atrazine to be used until the 10th Sept. 2005; in 4 countries (ES, GB, IE & PT) Atrazine may be allowed to be used until the 31st Dec. 2007 for specifically listed uses ref, Annex in the above mentioned Commission decision. This restriction can be considered to be the ultimate source control option for reduction of Atrazine concentrations in the aquatic environment.

Despite this legislation Atrazine is still present in soil, groundwater, surface water and drinking water wells. There are several end-of-pipe techniques for reducing Atrazine from water. These end-of-pipe measures are presented below.

Table 1: Emission sources and possible emission abatement measures

	Sources:	Groundwater	Surface water	Waste water
	Applicability:	For the production of drinking water and groundwater treatment at remediation sites	For the production of drinking water	Sewage water treatment plant
	1 Powdered Activated Carbon	X	X	X
	2 Granular Activated Carbon	X	X	X
	3 Chemically activated Fibres	O	O	O
	4 Ozone	X	X	X
	5 AOP (Ozone/H_2O_2)	X	X	X
End-of-Pipe measures	6 Ozone + Pt-catalyst	O	O	O
	7 UV	X	X	X
	8 AOP (UV/H_2O_2)	X	X	X
	9 UV/TiO_2	O	O	O
	10 Stepwise Fenton Process	O	O	O
	11 Nanofiltration (NF)	X	X	X
	12 Reverse Osmosis (RO)	X	X	X

Note: X = available measure; O = emerging measure

Table 2: Measure / source solutions under assessment

Measure / source	Assessment				Remarks
	Technical feasibility	**Performances**	**Costs**	**State of the art**	
Powdered Activated Carbon (PAC)	*Total score:* +	*Total score:* ++	*Total score:* +	*Total score:* ++	PAC must be removed by filtration or sedimentation
	Pol.: diffuse *Rge:* low *Cnd.:* NOM *Lim.:* no	*Eff.:* 50-80 % *Oth.:* medium *En.:* low *CE:* Adsorption of DBP. *W:* high	*IC:* low *OC:* medium	*St:* BAT *App:* numerous	
Granular Activated Carbon (GAC)	*Total score:* +	*Total score:* ++	*Total score:* -	*Total score:* ++	GAC must be regenerated after a specific time by steam or heat.
	Pol.: diffuse *Rge:* low *Cnd.:* NOM *Lim.:* no	*Eff.:* 20-50 thousand bed volumes *Oth.:* low *En.:* low *CE:* Adsorption of DBP and biological breakdown of organic carbon. *W:* medium	*IC:* medium *OC:* medium	*St:* BAT *App:* numerous	
Chemically Activated Carbonfibres (CAF)	*Total score:* +	*Total score:* ++	*Total score:* --	*Total score:* --	Technique in development
	Pol.: diffuse *Rge:* low *Cnd.:* n.a. *Lim.:*	*Eff.:* Higher than GAC *Oth.:* low *En.:* n.a. *CE:* Adsorption of DBP *W:* medium	*IC:* hgh *OC:* high	*St:* emerging *App:* low	
Ozone	*Total score:* 0	*Total score:* -	*Total score:* 0	*Total score:* 0	ozone generators requires skilled technicians and regular maintenance
	Pol.: diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 20-50 % *Oth.:* disinfection and other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*IC:* high *OC:* medium	*St:* existing technique *App:* few	
Ozone/H_2O_2	*Total score:* +	*Total score:* 0	*Total score:* -	*Total score:* -	Ozone/H_2O_2 is a complex process and ozone generators requires skilled technicians and regular maintenance
	Pol.: diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 50-60 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*IC:* high *OC:* medium	*St:* existing *App:* few	
Ozone/	*Total score:* +	*Total score:* 0	*Total score:* 0	*Total score:* -	Technique in

Pt-catalyst (TiO$_2$)	*Pol.:* diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 93 % in 30 minutes *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* medium	*IC:* n.a. *OC:* n.a.	*St:* emerging *App:* low	development
UV	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low turbidity *Lim.:* no	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*Total score:* **+** *IC:* high *OC:* Low	*Total score:* **-** *St:* Existing *App:* few	High capacity necessary to achieve enough breakdown of Atrazine
UV/H$_2$O$_2$	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low turbidity, low NOM *Lim.:* no	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*Total score:* **+** *IC:* high *OC:* Low	*Total score:* **-** *St:* excising *App:* few	
Stepwise Fenton Process	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Total score:* 0 *Eff.:* 35 % in 5 minutes *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* mdium	*Total score:* **-** *IC:* high *OC:* Medium	*Total score:* **--** *St:* emerging *App:* few	Technique in development
Nano-filtration (NF)	*Total score:* **++** *Pol.:* diffuse *Rge:* low *Cnd.:* no chlorine *Lim.:* depends on pore size	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* many *En.:* high *CE:* *W:* high	*Total score:* **--** *IC:* high *OC:* high	*Total score:* **+** *St:* BAT *App:* numerous	frequently already a treatment step of a drinking water plant
Reverse Osmosis (RO)	*Total score:* **++** *Pol.:* diffuse *Cmp.:* *Cnd.:* no chlorine *Lim.:* no	*Total score:* **++** *Eff.:* 80-100 % *Oth.:* many *En.:* high *CE:* *W:* high	*Total score:* **--** *IC:* medium *OC:* high	*Total score:* **+** *St:* BAT *App:* numerous	frequently already a treatment step of a drinking water plant

Scores (five levels): **– –** for very bad; **–** for bad; **o** for average; **+** for good; **++** for very good;
Sub-criteria (with possible values): *Pol.* = Type of pollution (point source, diffuse); *Rge* = Range of concentration (small, medium, wide); *Lim.* = Limits and restrictions (low, medium, high); *Cmp.* = Complexity of implementation (low, medium, high); *Imp.* = Impact on the process, on the factory (low, medium, high); *Eff.* = Efficiency of emission reduction (in %); *Oth.* = Removal of other pollutants (list of other pollutants removed); *En.* = Consumption of energy (no, low, medium, high); *CE* = Cross-effects (list of cross-effects); *W* = Production

of waste (list of waste); *IC* = Investment costs (no, low, medium, high); *OC* = Operational costs (no, low, medium, high); *St.* = Status of the technique (BAT, existing, emerging); *App.* = Number of applications (none, some, numerous).

2. Introduction

The overall objective of this document is the inventory and assessment of technical options for reducing the water emissions of **Atrazine** in Europe. Options include end-of-pipe techniques (e.g. waste water treatment) and process-integrated technical options (e.g. substitution or closed-circuit operation). The document aims to identify main uses and emission sources for **Atrazine** and to assess in terms of costs, effectiveness, and feasibility the technical means to abate emissions in water. It has been developed to give stakeholders a background material and an overview of possible reduction options at the European scale in the perspective of future emission reduction strategies to be developed.

The document is a result of project SOCOPSE which is a European research project funded by the EU 6th framework program for research. The goal of this project is to support the implementation process of the Water Framework Directive by providing guidelines and decision support system for the management of priority substances.

The scope of the document is the pollution in continental waters. It covers the most important sectors responsible for direct and indirect emissions, discharges and losses to aquatic environment in Europe. Therefore, the control of pollution to air and land is out of the scope, and polluted air and land will be considered only as potential sources of pollution to water.

The document was prepared as follows. The identification of main uses and emission sources for **Atrazine** was achieved in a separate project task based on literature review and expert judgement. Here are reported the main conclusions.

As concerns the assessment of technical options, a literature review was conducted on both existing and emerging options to abate emissions to water. At the same time a survey was carried out with the main contributors to emissions to evaluate the options applied or considered in practice. Both information sources were compared and compiled in a first draft document which then was sent to stakeholders and debated during a one-day technical workshop. A second draft document included the workshop remarks. The final document takes into account the results of case studies conducted at the latter stages of project SOCOPSE.

Survey questionnaire, list of contacted organisations and list of participants to workshop are attached in appendices.

The document plan is as follows. Section 3 gives general information on **Atrazine**. Section 4 presents results on main uses and emissions of the substance. Section 5 reviews the technical options to reduce emissions, with a synthesis in Section 6. Section 7 concludes the document, with acknowledgements in Section 8 and references in Section 9.

3. General information

3.1 Presentation of the substance

Atrazine is an herbicide that does not occur naturally. Pure atrazine is an odourless, white powder that is not very volatile, reactive, nor flammable and that will dissolve in water. Atrazine is used to kill weeds, primarily in agriculture, but has also been used on highways, railroads, forestry, orchards, "Industrial Weed Control", private use in gardens and uses as a biocide (algal control).

Atrazine belongs to the group of "chlorotriazines" and was first made by Ciba Geigy in 1960, but it has also been produced after course expiry of the patent by a number of other companies. Because of the low cost price, atrazine rapidly became one of the most used herbicides in agriculture, especially form the cultivation of corn. In the United States it was for a long time the most used herbicide in agriculture, with an annual usage of more than 30 million kilogram. Around the year 2000 it was outdistanced by the product Glyphosphate.

Atrazine can contaminate the ground and surface water when it is washed from the soil by rainfall or irrigation. When atrazine enters the water it can stays there for a long time because the breakdown of the chemical is very slow. Furthermore a median DT50 of 43 days was calculated days based on 61 field trials in a range of countries (Austria, Germany, France, Switzerland and the USA (Minnesota to California); which demonstrate that Atrazine is degraded quite rapidly under a wide range of normal use conditions (ref. 3rd addendum to the Draft assessment Report). It is possible that under certain conditions Atrazine is degraded more slowly, but is generally not in normal use conditions.

Moreover some types of weeds developed after course of time resistance against atrazine, so the effectiveness of the product diminished.
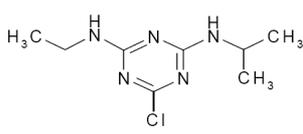
The European Commission decision 2004/248/EC not to include Atrazine on Annex I to Directive 91/414/EC specify phase out of the use in the EU. According to Article 3 all Member States except 4 could allow Atrazine to be used until the 10th Sept. 2005; in 4 countries (ES, GB, IE & PT) Atrazine may be allowed to be used until the 31st Dec. 2007 for specifically listed uses ref, Annex in the above mentioned Commission decision.

3.2 Classification and labelling

In Table 3 and Table 4 the chemical and physical information on Atrazine is summarized respectively. TTable 5 shows the toxicological and CMR classification.

Table 3: Chemical information on Atrazine

Characteristic	Information	Reference
Chemical name:	Atrazine	EPA 1983; Howard 1991
Synonyms:	6-Chloro-n-ethyl-n'-(1-methyl ethyl)-triazine-2,4-diamine; 2-Chloro-4-ethylamino-6-isopropylamine-s-triazine; 2-Chloro-4-(ethylamino)-	

	6-(isopropylamino)-s-triazine; 2-Chloro-4-(ethylamino)-6-(isopropylamino)-triazine; Chloro-4-(propylamino)-6-ethylamino-s-triazine; Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine; Butyl-n-(acetyl)-aminopropionic acid	
Registered trade names:	Aatrex®, Aatram®, Atratol®, Gesaprim®	EPA 1983; Syngenta 2000
Chemical structure:		
Identification numbers: CAS NIOSH RTECS DOT/UN/NA/IMO	registry 1912-24-9 XY5600000 UN 2763 UN 2997 UN 2764 UN 2998 IMO 6.1 IMO 3.2 HSDB 413	HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002 HSDB 2002
Experimental code number	G-30027 (Ciba-Geigy)	Farm Chem Handbook 2001

CAS = Chemical Abstracts Services;
DOT/UN/NA/IMCO = Department of Transportation/United Nations/North America/International Maritime Dangerous Goods Code;
EPA = Environmental Protection Agency;
HSDB = Hazardous Substances Data Bank;
NIOSH = National Institute for Occupational Safety and Health;
RTECS = Registry of Toxic Effects of Chemical Substances

Table 4: Physical information on Atrazine

Property	Information	Reference
Molecular weight	215.69	HSDB 2002
Color	White colorless	HSDB 2002
Physical state	Colorless powder Colorless crystals	IARC 1999 Verschueren 2001
Melting point	173–175 °C	HSDB 2002
Density	1.23 g/cm^3 (22 °C)	HSDB 2002
Odor	Odorless	NIOSH 1994
Solubility in water at 22 °C	34.7 mg/L	Ward and Weber 1968
Partition coefficients: Log K_{ow}	2.60 2.71	Hansch et al. 1995 Brown and Flagg 1981
Log Koc	1.96 1.97 2.98 3.38	Dousset et al. 1994 Green et al. 1993 Koskinen and Rochette 1996 Koskinen and Rochette 1996

	2.18	Meakins et al. 1995
	2.53	Meakins et al. 1995
	2.33	Weber 1991
Vapor pressure at 25 °C	2.89×10^{-7} mmHg	Tomlin 1997
Henry's Law constant at 25 °C	2.96×10^{-9} atm-m^3/mol	Riederer 1990
pK$_a$	1.68	Bailey et al. 1968
Hydrolysis rate constant at 25 °C	2.735×10^{-11} cm^3/molecule-second (estimated)	Meylan and Howard 1993
Auto ignition temperature	No data	
Flashpoint	Not applicable	EPA 1983
Flammability limits	Not applicable	EPA 1983
Conversion factors	mg/m^3 = 8.82 x ppm	HSDB 2002; IARC 1999
Explosive limits	Not applicable	EPA 1983

Table 5: Toxicological and CMR classification of Atrazine

R-phrases and Labelling	Reference
Xn; N, R48/22 – R43 – N; R50-53	ESIS
Xn: harmful	ESIS
R43 May cause sensitization by skin contact	ESIS
R48/22: Harmful: danger of serious damage to health by prolonged exposure if swallowed	ESIS
N: dangerous for the environment	ESIS
R50/53"Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	ESIS
Classification CMR	
no carcinogenic effects, classification with N	ECB Ispra, 2000

3.3 Regulations and controls for the substance

The EU Council Directive 91/414/EEC regulates the placing of plant protection products on the market. The European Commission decision 2004/248/EC not to include Atrazine on Annex I to Directive 91/414/EC specify phase out of the use in the EU. According to Article 3 all Member States except 4 could allow Atrazine to be used until the 10th Sept. 2005; in 4 countries (ES, GB, IE & PT) Atrazine may be allowed to be used until the 31st Dec. 2007 for specifically listed uses ref, Annex in the above mentioned Commission decision.

4. Production, uses and emissions

4.1 Production and uses

a) Production

Atrazine is produced by a continuous process in which isopropylamine reacts with cyanuric acid under basic conditions, forming 2,4-dichloro-6-isopropylamino-s-triazine, that reacts with monoethylamine and dilute caustic to form atrazine. The approach allows for continuous product recovery, solvent recycling, and waste removal (IARC 1999; UDC 1977). The triazine herbicides were first synthesized in 1955 (Kroschwitz and Howe-Grant 1995) and atrazine was first registered for use by the Ciba-Geigy Corporation in 1958 (Ribaudo and Bouzaher 1994). It has been used as an effective broad-leaf herbicide in corn, sorghum, and sugar cane, and has also been used for other crops and for non specific treatment of weeds along railways, highways, forestry, orchards, "Industrial Weed Control", private use in gardens and uses as a biocide (algal control).

b) Uses

Atrazine is used on crops such as sugarcane, corn, pineapples, sorghum, and macadamia nuts, and on evergreen tree farms and for evergreen forest regrowth. It has also been used to keep weeds from growing on both highway and railroad the other applications as mentioned above. It should be used at the appropriate application rates, which have been reduced to 1.4–2.0 pounds per acre (Johnson et al. 1996).
Atrazine can be sprayed on croplands before crops start growing and after they have emerged from the soil.

Atrazine is available in powder, liquid or granular but can not applied in this form. Certified herbicide workers diluted the purchased atrazine in water and spayed the dilution on crops or croplands. Atrazine is usually used in the spring and summer months. For it to be active, atrazine needs to dissolve in water and enter the plants through their roots. It then acts in the shoots and leaves of the weed to stop photosynthesis. Atrazine is taken up by all plants, but in plants not affected by atrazine, it is broken down before it can have an effect on photosynthesis. The application of Atrazine to crops as an herbicide accounts for almost all of the Atrazine that enters the environment, but some may be released from manufacture, formulation, transport, and disposal.
Atrazine has gained much attention because its frequent detection in surface and ground water supplies. In Europe atrazine consumption has dropped markedly since 1989 due to restrictions on its use and competition from newer, less-persistent herbicides.

4.2 Emissions

a) Sources of emissions to the air

1. When exposed to the atmosphere after field application to the soil or leaves surface, a fraction of Atrazine can volatilize and reach the atmosphere as a gas (2% of the applied atrazine)
2. The droplets emitted from the spay nozzles can evaporate before reaching the soil or the plant surface

3.   Transport at long distances by the wind during drift
4.   Due to the wind erosion process, wind can remove soil particles with pesticide molecules fixed on them from the soil surface

Discussion:
In some cases in the United States atrazine was measured in the air near its agricultural or other applications. It was only found in the atmosphere during the first month following the application of the herbicide to crops (Elling et al. 1987). In other cases, it was found until 4 (Chevreuil et al. 1996) to 8 months afterwards (Wu 1981). The manner in which atrazine is applied to the fields may influence its entry (i.e., volatilization) to the atmosphere. Cumulative volatilization of atrazine from conventionally- tilled fields was equal to 14% of the amount applied, but only 9% of the total applied amount was volatilized from notill fields (Weinhold and Gish 1994). Glotfelty et al. (1989) measured the volatilization of atrazine and other pesticides from moist and dry soils, and found that 2.4% of the applied atrazine had volatilized after 21 days.
Air concentrations of atrazine vary with application season; concentrations usually range from just above the detection limit of ~0.03 ng/m^3 to more typical concentrations of 0.20–0.32 µg/m3 (Trochimowicz et al. 2001).

b) Sources of emissions to the terrestrial ecosystem

1.   Field and non crop use applications
2.   Absorbed by crop
3.   Degraded by bacterial oxidation or chemical hydrolysis
4.   Adhered to soil particles

Discussion:
Atrazine may be commonly agricultural found in soils following use application for several weeks to a few years. However, in most cases, atrazine will be broken down in the soil over a period of one growing season. In addition to being removed from soil, atrazine is also taken up by the plants that grow there. This uptake is the first step in killing weeds. Atrazine may also be found in soils as a result of its manufacture, formulation, and disposal.

Experimentally-measured adsorption coefficients (log K_{oc}) for atrazine range from 1.96 to 3.38. However, studies have not demonstrated a relationship between the measured log K_{oc} and organic matter content (Dousset et al. 1994; Koskinen and Rochette 1996; Weber 1991). This suggests that the adsorption of atrazine to soil is influenced by processes other than interactions with soil organic matter, such as interactions with clays or coatings on quartz minerals. Koskinen and Rochette (1996) observed this type of disparity between the Koc of atrazine and soil moisture variations, and suggested that different types of interactions occur under different moisture regimes. Changes in the test conditions allowed for different interactions to occur between the atrazine and the clay minerals and soil organic matter. Wetting and drying cycles also enhanced the sequestration of atrazine in soil samples compared to those in which atrazine was exposed to continuous moisture (Kottler et al. 2001).

Following application to crop soils, as a result of sorption, most atrazine is found at highest concentrations in the upper layers of soil, (Koskinen and Clay 1997). Atrazine's rate of transport is dependent on many soil factors including the soil type, the amount of water that is

applied to the soil, the presence of crop residues, and the types of fertilizers used. Soil pH may also affect the transport of atrazine.

Atrazine sorption to soils increased with pH decreasing from 7.5 to 5.6 in a study of 10 Danish aquifer materials (Madsen et al. 2000). However, its mobility through soils, especially through macropores, has been demonstrated. In comparison to two other triazine herbicides (simazine and ametryn), atrazine turned out to be the most mobile in subtropical soils (Wang et al. 1996). Furthermore, the active ingredient of the applied herbicide moves more rapidly through soils than its breakdown products (Tasli et al. 1996). Its transport has been shown to occur along roots or through earthworm burrows (Koskinen and Clay 1997). In soils where mobile colloids are present, atrazine may be adsorbed and carried through preferential flow-paths in the soil and finally into groundwater (Sprague et al. 2000).
Atrazine does not tend to accumulate in living organisms such as algae, bacteria, clams, or fish, and, therefore, does not tend to build up in the food chain.

c) Sources of emissions to the aquatic environment

1. Leaching below root zone by rain or irrigation
2. Surface run off to lakes and rivers
3. Atmospheric deposition on the water surface by rainfall
4. Discharges in sewage effluents or storm water as a result of run off from buildings and construction in paved urban areas
5. Drainage and deep groundwater
6. Industrial activities: production of atrazine

Discussion:
Atrazine is removed from air mainly by rainfall. When atrazine is adsorbed on dust particles, the wind can blow it long distances from the nearest application area. For example, atrazine has been found in rainwater more than 180 miles (300 kilometers) from the nearest application area (Thurman and Cromwell 2000; Thurman et al. 1995).

Any atrazine that is washed from the soil into streams (e.g. river) and other bodies (e.g. groundwater) of water will stay there for a long time, because breakdown of the chemical is slow in rivers and lakes. When atrazine is deposited into aquatic matrices, some is expected to remain in the water column and some is expected to partition into the sediments. Atrazine has a measured log octanol/water partition coefficient (log Kow) of 2.6–2.71 (Brown and Flagg 1981; Hansch et al. 1995) and has a solubility in water of 34.7 mg/L (Ward and Weber 1968).

Atrazine has been shown to be relatively mobile in soils (Redondo et al. 1997; Southwick et al. 1995). In a silt loam soil, atrazine migrated almost as quickly as the conservative bromide tracer (Starr and Glotfelty 1990). Also is Atrazine in the 1960's to the 1980's uses for very high application rates compared to what has used the most recent years and that the product for some uses e.g. forestry and IWC often was used in the autumn and winter where degradation in the soil is slower (temperature related) combined whit the fact this is also the period where the recharge of groundwater aquifers occur. By this reasons atrazine is commonly found in groundwater and as a contaminant of drinking water wells.

Atrazine degradation in surface waters is slow, and its biodegradation in surface waters is demonstrated. A halflife time of Atrazine is shown 55-100 days (Council Directive

91/414/EEC, 1996). It has been shown to have long residence times in the water column of lakes and streams, with half-lives >200 days. Photolysis of atrazine has not been demonstrated in water, unless substantial amounts of dissolved organic matter of acidic conditions are present (Curran et al. 1992; Penuela and Barcelo 2000). Atrazine degradation in surface waters appears to be primarily due to abiotic hydrolysis (Feakin et al. 1994), and losses from small streams were also best explained by an abiotic mechanism (Kolpin and Kalkhoff 1993).

Adrian and Suflita (1994) observed no anaerobic degradation of atrazine in aquifer slurries. No degradation of atrazine was observed in an alluvial gravel aquifer over a distance of 90 m and a period of 49 hours. Atrazine concentrations were significantly reduced in batch tests over a period of 194 days; however, analysis suggests that the degradation is from chemical reduction and not biodegradation (Pang and Close 1999). Atrazine was degraded in the aqueous phase above anaerobic soil with a half-life of 86 days, under strongly reducing conditions (Seybold et al. 2001). Biodegradation has been shown only to occur when pure cultures of atrazine degraders are isolated from water or soil samples and grown in the laboratory; the activities of these organisms in the laboratory, however, have little or no relevance to natural aquatic biodegradation processes. Therefore, it appears that biodegradative losses of atrazine in aquatic systems are negligible.

5. Options for reducing emissions: detailed information

5.1 Source control options

a) Process-oriented options

There is no more production of atrazine in Europe.

b) User-oriented options

The use of atrazine in the European Community is no longer allowed due to the commission decision of March 10th 2004. This can be considered to be the ultimate source control option for reduction of atrazine concentrations in the aquatic environment.

c) Alternatives options

Atrazine has already been substituted.

5.2 End-of-pipe options for the substance

In this paragraph End-of-pipe techniques which can be used to remove **Atrazine** from wastewater by an industrial or municipal waste water plant and from surface or groundwater for production of drinking water will be described. The techniques are based on:

- Adsorption

- Photolysis / oxidation

- Physical separation

Many evaluations in this paragraph (e.g. activated carbon and ozone) are based on the use of the methods in drinking water production. This is due to the fact that Atrazine sometimes can be found in very low concentrations in sources for the production of drinking water. As the presence of Atrazine in the finished product is not acceptable, drinking water companies were obliged to extend their existing water treatment systems with new technology to remove organic micro pollutants.

a) Adsorption on activated carbon

(i) Description[1]

The activation process for the manufacture of activated carbon creates highly porous materials with a distribution of pore sizes and surface areas. Depending upon the activation process and base material, activated carbons also have a distribution of surface functional groups that

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[1] More information is available in the report *Fact sheets for end-of-pipe options*.

influence their adsorption characteristics. Activated carbon primarily removes natural organic matter (NOM) and synthetic organic compounds (e.g., pesticides like Atrazine and chlorinated solvent) from water through hydrophobic interactions between the organics and the activated carbon surface. Contaminations are adsorbed by attraction to and accumulation within the activated carbon. Pore structure, as defined by the distribution of pore size, has a large influence on both adsorption capacity and adsorption kinetics. An appropriate distribution of mesopores (20-500 Å) and micropores (< 20 Å) will increase the adsorption capacity for organic contaminations. Those contaminants with low aqueous solubility, and a size conducive to fitting within the pore structure, are most readily adsorbed by activated carbon. In drinking water treatment, the concentration and type of NOM in the source water will compete with contaminants for surface adsorption sites, thus NOM can reduce the effectiveness of activated carbon (AWWA, 2007).

There are three types of activated carbon commercially available: Granular Activated Carbon (GAC), Powdered Activated Carbon (PAC) and Chemical Activated Carbon-Fibers (CAF).

(ii) Technical feasibility (applicability)

In a treatment plant the common points for addition of PAC include the plant intake, rapid mixer and filter influent. The main advantages of PAC are the continuously providing of fresh carbon and the possibility to use it seasonally when risk of trace organics may be greater. The PAC can be removed after a certain retention time by filtration or sedimentation. PAC can not be regenerated.

GAC is commonly used as a biological filter for TOC-removal and as an adsorption filter for removal contaminants. In these filters, the activated carbon is present as granulates having a diameter of 0.8-1.5 mm. These granulates have a highly porous structure, thus creating a very large surface area (400 m^2/g). The water flows (from above) through the bed of granules, making the micropollutants adsorb to the surface. Because of the surface forces of the granules, these pollutants are transported inwards, decreasing the load at the grain surface.
After the filter has been used for treating several thousands bed volumes of water, it will no longer adsorb any pollutants, a process referred to as breakthrough. This breakthrough differs across the compounds to be adsorbed. When the filter bed is saturated with pollutants, the filter material is removed and can be regenerated.

Activated carbon can be operated at various conditions. Important factors that effect efficiency of activated carbon are the quality, particle size, contact time, interactions with chemical oxidants (chlorine), concentration of permanganate, alkalinity, coagulants and the concentration and type of organic compounds. Special attention should be paid to remove suspended solids and easily removable organic compounds (NOM) from the influent of the GAC-filter. Suspended solids can cause the filter bed to clog. Easily removable organic compounds will block the adsorption sites on the activated carbon, on which organic micropollutants or pesticides are to be adsorbed.
In a study (Bernazeau *et al.*, 1996) this effect was investigated using Atrazine as test pollutant and respecting the dissolved organic matter (DOC) and Atrazine concentration ratio found in natural waters. It was found that the impact on competitions with micropollutants not only depends on the level of DOC, but also the type of organic matter. In the case of Atrazine adsorption onto activated carbon, its performance can be predicted from polyhydroxyaromatic compound levels in the water.

Considering filters of the same size, the pumping costs for activated carbon filters are similar to the cost for depth filters. Regeneration of the activated carbon is an energy intensive process, consuming between 1 – 3 kWh/m3 for the reactivation process alone. (Jong, 2005)

Emerging adsorbent-based technologies:
In a study Chemically Activated Carbonfiber (CAF) is tested for the adsorption of Atrazine (Yue *et al.*, 2005). The adsorption isotherm shows that the CAF has a higher adsorption capacity than GAC. Breakthrough curves for both CAF-filter and GAC-filter show that the CAF-filter has greatly improved effectiveness of adsorption and have a higher effectiveness in the selective adsorption of Atrazine (50 times higher) than the GAC-filter.
Another emerging technology is Moving Bed Absorption (MBA), which combines a dynamic sand filter with counter current carbon adsorption In one single treatment step.The functionality and economic attractiveness of this technology for the polishing of wastewater effluents is claimed by TNO. MBA is currently tested and evaluated in the Netherlands.

Performances (environmental effectiveness)

Technique	Removal	Conditions	Reference
PAC	50-80%	5 mg PAC/l, 4-5 hour contact time	AWWA, 2007
GAC	20,000-50,000 bed volumes	to 10 % breakthrough	AWWA, 2007

The ability of PAC to remove organic contaminants depends upon PAC dosage and contact time, as well as the molecular structure and behaviour of the contaminants of interest. GAC also was found to be highly-effective; however, water soluble contaminants (such as Atrazine) can breakthrough the GAC much more rapidly than strongly bound hydrophobic contaminants. Stream treated CAG has significantly greater adsorption capacity as shown by the increase in bed volumes passed prior to contaminants breakthrough. Fresh GAC is highly effective to remove trace of organic contaminants, while GAC that is not regularly replaced/regenerated relatively ineffective.

(iii)   Costs (of Compliance)

The most important component of the cost using PAC is the cost of the PAC itself (AWWA, 1994). The cost of PAC is € 2.0 and 2.5 per kg (Hydrotec, 2006). For a removal of 50-80 % the costs for PAC range from 0.010-0.015 €/m^3. Total costs are estimated to be 0.015 – 0.020 €/m^3 including dosage equipment and excluding a filtration/sedimentation step that is needed to remove the PAC.(DHV, 2002) The costs for filtration/sedimentation have to be added if PAC-treatment can not be integrated in an existing treatment system.

The treatment costs of GAC depend on the quality of the water (organic load) and the contact time for removing the contaminant. The treatment cost for a contact time between 10 and 20 minutes are 0.10-0.15 €/m^3 for capacities between 200-1000 m^3/h (DHV, 2002). The contact time for the removal of Atrazine in a waste water treatment plant shall be higher, because of the higher organic load of waste water.

(iv)   State of the Art

PAC and GAC are considered BAT for the removal of Atrazine from water streams.

b) Oxidation by ozone, hydrogen peroxide and AOP

(i)   Description

Ozone (O_3) is a strong oxidant and disinfectant. Ozone decays rapidly within minutes after addition to water and results in the formation of fewer halogenated organic disinfection by-products. Ozone reacts with organic contaminants through either the direct reaction with molecular ozone or through the formation of free radicals, including the hydroxyl radical (HO•). The formation of HO• occurs through a series of promotional steps, which involve initiators such as hydrogen peroxide, ultra violet radiation, natural organic matter or hydroxide ion. Both molecular ozone and hydroxyl radical pathway can lead to transformation of organic compounds.

In most water treatment applications, the concentration of hydroxyl radicals is extremely low. In order to increase the transformation of recalcitrant micropollutants, advanced oxidations processes (AOP) are applied to increase HO• concentrations. In most Ozone AOP applications, Hydrogen peroxide (H_2O_2) is added to promote the initiation step in ozone decomposition that will lead to higher radical production. The overall kinetics of the ozone decomposition is dependent on water quality parameters (alkalinity, pH and NOM).

More information is available in the section "Chemical oxidation" in the report *Fact sheets for end-of-pipe options*.

(ii)   Technical feasibility (applicability)

Ozone is mostly generated by corona discharge. Because ozone is an unstable molecule, it should be generated at the point of application for the use in water treatment. For the production of ozone dry air or pure (liquid)oxygen can be used.

The voltage required to produce ozone by corona discharge is proportional to the pressure of the source gas in the generator and the width of the discharge gap. Theoretically, the highest yield (ozone produced per unit area of dielectric) would result from a high voltage, a high frequency, a large dielectric constant, and a thin dielectric.

For the production of 1 kg ozone theoretically 2.9 MJ (0.8 kWh) is necessary. In practice the energy consumption is 6 to 8 times higher.

The specific amount of ozone for the treatment of contaminants in the water depends on the organic load, pH, alkalinity and temperature. Typical ozone operating parameters for the removal of contaminants are:

- Transferred ozone dose (mg/L)   2.29
- Ozone demand (mg/L)   0.91
- Half life (min.)   3.74
- Ozone Decay Rate   -0.186
- CT (mg-min/L)   4.77

Ozone and H_2O_2 delivery systems are complex using highly technical instruments, however the processes are highly automated and reliable, requiring only a modest degree of operator skill and time to operate them. Ozone generators require regular maintenance by skilled technicians (Jong, 2005).

(iii) Performances (environmental effectiveness)

Technique	Removal (%)	Conditions	Reference
Ozone (O_3)	20-50 %	1.0-1.2 mg O_3/L and 24 minutes contact time	AWWA, 2007
Ozone/H_2O_2	50-60 %	1.2-2.6 mg O_3/L, 0.0625 mg H_2O_2/L, 24 min. contact time	AWWA, 2007

Although ozone is highly efficient for contaminant oxidation, it should be noted that oxidation by ozone generally does not result in complete mineralization. Therefore (undesired) oxidation products should be expected. The organic oxidation products from ozone treatment in general are biodegradable and thus may be removed during subsequent biological filtration. Maldonado et al. (2006), reported the very slow oxidation of Atrazine by Ozone. For a solution with 15 mg/L Atrazine and an ozone concentration of ±10 mg/L a breakdown of 50% was measured after 85 minutes and 100 % after 150 minutes.

The removal of Atrazine by AOP was similar to ozone alone. The addition of hydrogen peroxide prior to ozonation generally improved removal by only 5-15% and accelerated the 2nd reaction rates. AOP should be considered when contact time is unavailable for destruction by ozone alone.

The Fenton Process (FP) is an Advanced oxidation Process (AOP) which combine H_2O_2 and ferrous water. In a study (Chu et al., 2007) the performance of the removal of Atrazine by conventional FP (one dosage of H_2O_2) with stepwise-FP (where the total dose of H_2O_2 was split and inputted into the system at different times and/or quantities) were compared. The conventional FP removes 25 % of Atrazine and the stepwise-FP than 35 % after 5 minutes contact time.

Emerging ozone-based technologies:
As described, ozone is not very effective in the removal of Atrazine from water. For this reason a study (Tepuš and Simonic, 2007) was carried out to the degradation of Atrazine by using a PT-catalyst (TiO_2) in combination with ozone. The result showed that after 30 minutes of catalytic ozonation up to 93% of Atrazine was removed, while only 33% of Atrazine was removed by ozonation alone.

(iv) Costs (of Compliance)
The costs of ozone treatment are dependant on the quality of the water (organic load) and the contact time for oxidation. For Atrazine removal of 20-50 % with a 24 minutes contact time the treatment cost are 0.05-0.10 €/m^3 for capacities between 200-1000 m^3/h (DHV, 2002).

For the combination of ozone/H_2O_2 the treatment costs are 0.06-0.11 €/m^3 for capacities between 200-1000 m^3/h (DHV, 2002).

(v) State of the Art
For the removal of Atrazine the treatment techniques ozone or ozone/H_2O_2 are not considered BAT.

c) UV irradiation and UV/hydrogen peroxide Oxidation

(i)   Description

Since early 1970's, ultraviolet (UV) light-based processes were identified as promising alternatives to conventional treatment technologies for organic pollutant removal from contaminated waters. UV-light oxidizes organics in water by two mechanisms. First, UV can directly cleave bonds in organic molecules by direct photolysis. Second, UV reacts with water or inorganic constituents in water to form highly reactive intermediates, with the formation of hydroxyl radicals (HO•) being the most important in oxidation of organic compounds. HO• radicals are highly reactive, non-selective oxidants that react with organic compounds. The presence of hydrogen peroxide (H_2O_2) can increase the concentration of HO• in solutions (H_2O_2 + UV $\rightarrow$ 2 HO•).

The energy of UV-C radiation (200-280nm) is often sufficient to break chemical bonds in organic compounds capable of absorbing those wavelengths. This process is considered direct UV photolysis, and its efficiency is strongly dependent on both contaminant and water quality.

UV advanced oxidation processes (AOP's) rely on the ability of certain chemicals dissolved in water (i.e. hydrogen peroxide) to absorb UV light and generate highly reactive species such as hydroxide radicals (HO•). Hydroxide radicals react indiscriminately with most organic pollutants. UV/H_2O_2 processes are currently applied in full-scale UV systems to remove recalcitrant contaminants and other organic compounds.

(ii)   Technical feasibility (applicability)

There are two types of UV lamps commercially available, the low pressure (LP) UV lamp (monochromatic light 254nm) and medium pressure (MP) UV lamp (polychromatic light 200-400nm). The LP-UV lamps have a specific energy output of 4-120 Watt, MP-UV lamps have a specific energy output of 400-10,000 Watt.

UV can be used in full stream or in side stream.

For effective UV treatmen, the water must have a low turbidity. Otherwise suspended solids will block the UV light. Also the water itself blocks UV light to some extent. The extent to which UV light is blocked differs for every type of water. It can be measured as UV transmission.

The radiation from a lamp decreases over time. This loss in radiation has to be compensated by other lamps or by an overdose. Most lamps have a lifespan of 6,000 hours.

The UV dose (D in mJ/cm^2 or mWs/cm^2) is the product of UV intensity (I in mW/cm^2 or W/m^2) and the residence time (t in seconds).

$$D = I \times t$$

For the use of UV/H_2O_2 it is very difficult to predict the efficiency of pollutant removal since results vary significantly with the specific oxidant in question and the characteristics of the treated wastewater (pH, temperature etc).

UV systems require skilled technicians and regular maintenance.

(iii)   Performances (environmental effectiveness)

Technique	Removal (%)	Conditions	Reference
UV	<20 %	UV-dose: 40 mJ/cm^2	AWWA, 2007
UV	50-80 %	UV-dose: 439 mJ/cm^2	AWWA, 2007
UV/H$_2$O$_2$	50-80 %	UV-dose: 372 mJ/cm^2, H$_2$O$_2$ at 5 mg/l	AWWA, 2007

In practice UV technology is mostly used for the disinfection of the water (40 mJ/cm^2). At this dosage UV will only remove a small number of target contaminants. For a contaminant to be oxidized by UV light, it must absorb light at the same wavelength as produces by the UV process.
The addition of H$_2$O$_2$ for advanced oxidation with UV increased the removal of Atrazine dependent on H$_2$O$_2$ dosage and UV fluency.

Emerging UV and/or H$_2$O$_2$-based technologies:
Another UV-based technique to remove Atrazine is the photocatalytic degradation by an immobilised TiO$_2$ film. This was investigated using immobilised TiO$_2$ films in a stirred tank reactor designed to maximise mass transfer (McMurray *et al.*, 2006). The degradation of Atrazine was demonstrated with a number of breakdown products identified including the stable end product cyanuric acid. 50% of the Atrazine was removed after 40 minutes and it was completely degraded after 150 minutes.

(iv)   Costs (of Compliance)

The costs of UV treatment depend on the quality of the water (TNU and transmission), the UV-absorbance of the specific contaminant (Atrazine) and the contact time. For a removal of 50-80 % with a UV dose of 440 mJ/cm^2 the treatment cost are 0.03-0.05 €/m^3 for capacities between 200-1000 m^3/h (DHV, 2002).

For the combination of UV/H$_2$O$_2$ the treatment cost are 0.04-0.06 €/m^3 for capacities between 200-1000 m^3/h (DHV, 2002).

(v)   State of the Art

Because of the relatively high energy cost, low removal efficiency and complex technique UV and UV/H$_2$O$_2$ are not considered BAT.

d) Physical separation by membrane filtration

(i)   Description

Membrane filtration separates contaminants from water based upon molecular size and/or electrostatic interactions with the membrane surface. Size, charge and hydrophobicity of pesticides emerge as critical characteristics influencing the removal effectiveness of filtration membranes.
Microfiltration (MF) and ultrafiltration (UF), both considered low pressure membranes, generally remove only those pesticides that adsorb onto colloids or particulates in the water. Pesticides can be removed by high-pressure membranes, such as reverse osmosis (RO) and tight nanofiltration (NF), commonly used for rejection of inorganic and organic contaminants

due to their smaller pore sizes and corresponding lower molecular weight cut-offs. The removal of organic compounds by RO and NF can be qualitatively predicted based on compound structure and membrane properties. More information is available in the section "Nanofiltration and Reverse Osmosis" in the report *Fact sheets for end-of-pipe options*.

(ii)   Technical feasibility (applicability)

Nanofiltration (NF) or Reverse osmosis (RO) semi-permeable membranes are used, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. Most NF/RO technology uses a process known as "cross flow" to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected species away from the membrane, in a concentrated brine reject water. The process of NF/RO requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases.

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 Dalton.

Pesticides rejection increases as the pH increases and can be affected by the presence of natural organic matter in the water. Variation of membrane, flux, pesticide solubility, charge, diffusion coefficient, or molecular weight and feed stream sulphate, sodium and chloride concentration do not significantly affect the pesticide rejection. (AWWA, 2000)

The waste streams from NF or RO membranes can be more complicated to dispose of or treat because of the higher concentration of Atrazine in the concentrate.

(iii)   Performances (environmental effectiveness)

Technique	Removal (%)	Reference
UF	<20 %	AWWA, 2007
NF	50-80 %	AWWA, 2007
RO	80-100 %	AWWA, 2000

The energy demand for membrane filtration depends on the water characteristics and ranges between medium and high levels.

Membrane treatment produces a waste stream (concentrated brine) of approximately 10 % of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the wastewater.

(iv)   Costs (of Compliance)

For a capacity between 200-1000 m³/h, treatment costs for NF and RO vary between 0.18-0.68 €/m³ depending on flux and recovery, excluding the costs of discharge or treatment of the concentrate (DHV, 2002).

Most membranes have a lifetime of 5 years. Depending on the scale/size of the installation, replacement costs are 15-25 €/m^2 membrane for capacities between 200-1000 m^3/h (DHV, 2002).

(v) **State of the Art**

Because of the high retention of (some) NF and RO membranes for Atrazine and their wide use, NF and RO are considered as BAT.

6. Options for reducing emissions: synthesis

Table 6 and Table 7 synthesise the main sources with the possible emission abatement measures, and the assessment of source abatement measures, respectively. For the assessment, all the measures are scored on four criteria: their technical feasibility, their performance, their costs, and their actual implementation (state of the art). For each criterion, the five possible scores are, in descending order: very good (++), good (+), average (o), bad (−), and very bad (− −). Note that each criterion is divided into a number of sub-criteria and the combination of sub-criteria gives the criterion score.

Table 6: Emission sources and possible emission abatement measures

	Sources	Groundwater	Surface water	Waste water
	Applicability	For the production of drinking water and groundwater treatment at remediation sites	For the production of drinking water	Sewage water treatment plant
Measures	1 Powdered Activated Carbon	X	X	X
	2 Granular Activated Carbon	X	X	X
	3 Chemically activated Fibres	O	O	O
	4 Ozone	X	X	X
	5 AOP (Ozone/H_2O_2)	X	X	X
	6 Ozone + Pt-catalyst	O	O	O
	7 UV	X	X	X
	8 AOP (UV/H_2O_2)	X	X	X
	9 UV/TiO_2	O	O	O
	10 Stepwise Fenton Process	O	O	O
	11 Nanofiltration (NF)	X	X	X
	12 Reverse Osmosis (RO)	X	X	X

Note: X = available measure; O = emerging measure

Table 7: Measure / source solutions under assessment

Measure / source	Assessment				Remarks
	Technical feasibility	**Performances**	**Costs**	**State of the art**	
Powdered Activated Carbon (PAC)	*Total score:* +	*Total score:* ++	*Total score:* +	*Total score:* ++	PAC must be removed by filtration or sedimentation
	Pol.: diffuse *Rge:* low *Cnd.:* NOM *Lim.:* no	*Eff.:* 50-80 % *Oth.:* medium *En.:* low *CE:* Adsorption of DBP. *W:* high	*IC:* low *OC:* medium	*St:* BAT *App:* numerous	
Granular Activated Carbon (GAC)	*Total score:* +	*Total score:* ++	*Total score:* -	*Total score:* ++	GAC must be regenerated after a specific time by steam or heat.
	Pol.: diffuse *Rge:* low *Cnd.:* NOM *Lim.:* no	*Eff.:* 20-50 thousand bed volumes *Oth.:* low *En.:* low *CE:* Adsorption of DBP and biological breakdown of organic carbon. *W:* medium	*IC:* medium *OC:* medium	*St:* BAT *App:* numerous	
Chemically Activated Carbonfibres (CAF)	*Total score:* +	*Total score:* ++	*Total score:* --	*Total score:* --	Technique in development
	Pol.: diffuse *Rge:* low *Cnd.:* n.a. *Lim.:*	*Eff.:* Higher than GAC *Oth.:* low *En.:* n.a. *CE:* Adsorption of DBP *W:* medium	*IC:* hgh *OC:* high	*St:* emerging *App:* low	
Ozone	*Total score:* 0	*Total score:* -	*Total score:* 0	*Total score:* 0	ozone generators requires skilled technicians and regular maintenance
	Pol.: diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 20-50 % *Oth.:* disinfection and other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*IC:* high *OC:* medium	*St:* existing technique *App:* few	
Ozone/H_2O_2	*Total score:* +	*Total score:* 0	*Total score:* -	*Total score:* -	Ozone/H_2O_2 is a complex process and ozone generators requires skilled technicians and regular maintenance
	Pol.: diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 50-60 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*IC:* high *OC:* medium	*St:* existing *App:* few	
Ozone/	*Total score:* +	*Total score:* 0	*Total score:* 0	*Total score:* -	Technique in

Pt-catalyst (TiO$_2$)	*Pol.:* diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Eff.:* 93 % in 30 minutes *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* medium	*IC:* n.a. *OC:* n.a.	*St:* emerging *App:* low	development
UV	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low turbidity *Lim.:* no	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*Total score:* **+** *IC:* high *OC:* Low	*Total score:* **–** *St:* Existing *App:* few	High capacity necessary to achieve enough breakdown of Atrazine
UV/H$_2$O$_2$	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low turbidity, low NOM *Lim.:* no	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* low	*Total score:* **+** *IC:* high *OC:* Low	*Total score:* **–** *St:* excising *App:* few	
Stepwise Fenton Process	*Total score:* **+** *Pol.:* diffuse *Rge:* low *Cnd.:* low NOM *Lim.:* no	*Total score:* **0** *Eff.:* 35 % in 5 minutes *Oth.:* disinfection and removal of other organic pollutants *En.:* medium *CE:* formation of AOC *W:* mdium	*Total score:* **–** *IC:* high *OC:* Medium	*Total score:* **– –** *St:* emerging *App:* few	Technique in development
Nano-filtration (NF)	*Total score:* **++** *Pol.:* diffuse *Rge:* low *Cnd.:* no chlorine *Lim.:* depends on pore size	*Total score:* **+** *Eff.:* 50-80 % *Oth.:* many *En.:* high *CE:* *W:* high	*Total score:* **– –** *IC:* high *OC:* high	*Total score:* **+** *St:* BAT *App:* numerous	frequently already a treatment step of a drinking water plant
Reverse Osmosis (RO)	*Total score:* **++** *Pol.:* diffuse *Cmp.:* *Cnd.:* no chlorine *Lim.:* no	*Total score:* **++** *Eff.:* 80-100 % *Oth.:* many *En.:* high *CE:* *W:* high	*Total score:* **– –** *IC:* medium *OC:* high	*Total score:* **+** *St:* BAT *App:* numerous	frequently already a treatment step of a drinking water plant

Scores (five levels): **– –** for very bad; **–** for bad; **o** for average; **+** for good; **++** for very good;
Sub-criteria (with possible values): *Pol.* = Type of pollution (point source, diffuse); *Rge* = Range of concentration (small, medium, wide); *Lim.* = Limits and restrictions (low, medium, high); *Cmp.* = Complexity of implementation (low, medium, high); *Imp.* = Impact on the process, on the factory (low, medium, high); *Eff.* = Efficiency of emission reduction (in %); *Oth.* = Removal of other pollutants (list of other pollutants removed); *En.* = Consumption of energy (no, low, medium, high); *CE* = Cross-effects (list of cross-effects); *W* = Production

of waste (list of waste); *IC* = Investment costs (no, low, medium, high); *OC* = Operational costs (no, low, medium, high); *St.* = Status of the technique (BAT, existing, emerging); *App.* = Number of applications (none, some, numerous).

7. Conclusion

The use of Atrazine in agriculture is forbidden in the European Community since March 10th 2004. By this legislation new emissions to water and soil stopped. This can be considered to be the ultimate source control option for reduction of Atrazine concentrations in the aquatic environment.

Before 2004 Atrazine was widely used in agriculture as an herbicide. Due to its high mobility in water Atrazine is commonly found in groundwater, surface water and as a contaminant in drinking water wells. Because the natural breakdown of the chemical is very slow it will stay there for a long time.

There are a number of possible end-of-pipe techniques available for reducing atrazine levels in water.
- Adsorption on Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC) and Chemically Activated Carbon Fibres. (CAF)
- Oxidation by ozone, UV or in combination with H_2O_2
- Separation by Nanofiltration (NF) or Reverse Osmosis (RO)

From the techniques mentioned above PAC, GAC, NF and RO can be considered as BAT.

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