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REMOVAL OF GLYPHOSATE BY WATER TREATMENT

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REMOVAL OF GLYPHOSATE BY WATER TREATMENT

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Identification of the performance of commonly used water treatment processes for removal of glyphosate from surface waters.

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- Provide an overview of the general requirements of water treatment, and principles of contaminant removal.
- Identify and summarise the relevant literature relating to removal of glyphosate by water treatment processes.
- Assess likely removal performance for defined treatment processes.

III REASONS

The EC Directive 98/83 related to the quality of water for human consumption sets a limit of 0.1 µg l^{-1} for pesticides, their relevant metabolites, decay and reaction products. This blanket standard applies to glyphosate, despite its very low toxicity. Aminomethylphosphonic acid (AMPA) is the only significant metabolite of glyphosate. It is produced very readily under environmental conditions, and is therefore usually included in reviews of glyphosate removal in water treatment. However, AMPA may also be present in surface waters from other sources.

IV CONCLUSIONS

Two of the most common oxidants used in water treatment, ozone and chlorine, can provide a high degree of removal (>95%) for glyphosate and AMPA under typical conditions used in water treatment. The majority of water treatment works use one (mainly chlorine) or both of these oxidants.

The most common water treatment process installed for removal of pesticides worldwide is adsorption using granular activated carbon (GAC). However, this does not provide an effective barrier to glyphosate or AMPA.

Other processes commonly used in water treatment (bankside or dune infiltration, coagulation/clarification/filtration and slow sand filtration) would each contribute some removal, but alone would not provide a secure barrier in relation to meeting a 0.1 µg l^{-1} standard.

Treatment process streams which include chlorine could deal with between 1 and 4 µg l^{-1} in the raw water to maintain less than 0.1 µg l^{-1} in the treated water, depending on the treatment processes used. If the treatment stream also includes ozonation, very much higher raw water concentrations of above 30 µg l^{-1} could be treated.

V   RECOMMENDATIONS

There is some evidence to suggest that virgin GAC provides adsorption of glyphosate and AMPA. On this basis, powdered activated carbon (PAC) may be more effective than GAC. It would be valuable to investigate this further through laboratory tests.

Because of the importance of oxidation for glyphosate and AMPA removal, it would also be valuable to investigate the impact of pH and temperature on the performance of chlorine, and the effect of temperature on ozonation performance. For both oxidants, maintenance of good performance and low water temperature (2°C) needs to be confirmed.

VI   RESUMÉ OF CONTENTS

This report provides an assessment of the likely performance of water treatment processes in relation to removal of glyphosate, based on a review of the literature and current understanding.

1. INTRODUCTION

Glyphosate (N-(phosphonomethyl)-glycin) is a broad spectrum, non-selective herbicide, widely used for the post-emergence control of annual and perennial weeds in a variety of applications. Glyphosate has a very low potential to reach groundwater due to strong soil binding properties and biodegradability in soil, but may reach surface water from indirect routes of entry such as spray drift, runoff and drainage, as well as point source contamination following poor agricultural practice.

In some countries, glyphosate is approved for aquatic and semi-aquatic uses, which involve direct application to weeds growing in surface water.

The authorisation procedures for pesticides include a risk assessment aimed at ensuring that concentrations will not exceed 0.1 μg l^{-1} in groundwater sources, when used in accordance with the specified application directions and realistic worst case use conditions.

The EC Directive 98/83 (1998) related to the quality of water for human consumption, sets a limit of 0.1 μg l^{-1} for pesticides, their relevant metabolites, decay and reaction products. This blanket standard applies to glyphosate, despite its very low toxicity. WHO have considered it unnecessary to derive a guideline value for glyphosate in drinking water. Aminomethylphosphonic acid (AMPA) is the only significant metabolite of glyphosate. It is produced very readily under environmental conditions, and is therefore usually included in reviews of glyphosate removal in water treatment. AMPA is chemically very similar to glyphosate and shows similar properties in terms of behaviour and low toxicity. However, there are additional likely sources of AMPA in surface water, originating from organic phosphonates, which are used as stabilisation agents in cooling waters and as adjuvants in detergents (Hopman *et al.*, 1995).

A considerable body of information is available on removal of glyphosate and AMPA by water treatment. WRc were asked to:

- Provide an overview of the general requirements of water treatment, and principles of contaminant removal.

- Identify and summarise the relevant literature relating to removal of glyphosate by water treatment processes.

- Assess likely removal performance for defined treatment processes.

A review of the UK Drinking Water Inspectorate reports (http://www.dwi.gov.uk/reports.shtm) for the last 5 years has shown that there have been only 4 failures of individual samples of drinking water to meet the pesticide standard for glyphosate, all in 2004, (Table 1.1). Three of these failures were for one water company, and the DWI report states that these may have arisen through contamination within the laboratory. Glyphosate is therefore not considered to be among the pesticides of particular concern in England and Wales. For comparison, failures for other pesticides are included in Table 1.1; glyphosate failures represent <2% of total number of pesticide failures.

Table 1.1   UK pesticide failures 2000 – 2005 (from DWI reports 2001-2006)

Pesticide	Number of failures	
	2000 - 2005	2005
MCPA	72	0
2,4-D	34	0
Mecoprop	31	4
Isoproturon	28	1
Propyzamide	22 (all in 2001)	0
Trietazine	16	9
Diuron	15	9
Atrazine	14	1
Carbetamide	13	0
Chlortoluron	13	1
Simazine	8	1
Glyphosate	**4 (all in 2004)**	**0**
Clopyralid	3	0
2,4,5-T	2	0
Carbophenothion	1	0
Metaldehyde	1	0
Chloridazon	1	0
Prochloraz	1	0
Dicamca	1	1
Total number of failures 2001-2005	280	27

2. REMOVAL OF ORGANIC MICROPOLLUTANTS BY WATER TREATMENT

2.1 Overview of water treatment requirements

The main requirement of drinking water is that it be free of pathogens and toxic chemicals. The prime objective of water treatment is disinfection, and one of the purposes of prior stages of treatment is to "prepare" the water for disinfection. For example, chlorine is the most commonly used disinfectant and unless materials causing turbidity (suspended solids) and colour (humic substances), which exert a chlorine demand, are removed from the water, the efficiency of disinfection may be impaired. Moreover, undesirable disinfection by-products may be produced, e.g. trihalomethanes (THMs), from the reaction of chlorine with humic substances.

Chlorination conditions used in water treatment for disinfection involve chlorine dosed in the range 2 - 4 mg l^{-1}, to provide a residual concentration of approximately 0.5 mg l^{-1} after a suitable contact time, usually between 0.5 and 2 hours. The dose required to maintain the desired residual depends on the nature of the water being treated.

The second most common oxidant used in water treatment is ozone. This is sometimes used as a disinfectant, but is more commonly used for removal of pesticides. Doses and residuals are similar to those for chlorine, but contact times are much shorter, usually less than 20 minutes. The higher reactivity of ozone compared with chlorine does not provide a long term residual, and chlorine is usually added to provide a more stable residual in distribution.

Chloramination of water, following disinfection, is also practiced at some sites, often where there is a need for greater persistence of chlorine in distribution, or to reduce formation of trihalomethanes (THMs). Monochloramines, which are formed by controlling the ratio of ammonia to chlorine, are less reactive with organic matter, including synthetic compounds.

Chlorine dioxide is used, though not widely in Europe, as an alternative to chlorine for disinfection. The benefits include effective disinfection with less pH dependency, improved oxidation of dissolved iron and manganese and reduced formation of disinfection by-products.

The selection of appropriate treatment processes or optimal combinations of processes is highly dependent on the quality of the raw water. Most groundwater sources are of a high quality and require minimal treatment, i.e. disinfection only. Surface waters generally contain higher levels of natural organic and inorganic materials, and are likely to contain relatively high concentrations of anthropogenic contaminants, which require removal.

Turbidity is caused by the presence of suspended matter such as clay, decaying vegetation and algae. Removal of turbidity may be achieved by filtration, either at high rates (rapid filtration) or at much lower rates using finer sand in the biologically mediated slow sand filtration process. Chemical coagulation can be used to cause the fine particles to agglomerate and be incorporated into chemical precipitates, forming large particles or floc which can be removed by rapid filtration, often with pre-treatment such as sedimentation or flotation. Commonly used coagulants are salts of aluminium or iron, sometimes in conjunction with polyelectrolytes.

Colour in natural waters is due mainly to organic matter originating from soils, particularly in peaty areas. Chemical coagulation is used to remove colour but the mechanism and conditions are different from those for turbidity removal, relying more on precipitation and/or adsorption of colour compounds on to the surface of floc. Because colour is relatively non-biodegradable and of a soluble or fine-colloidal nature, very little colour is removed by slow sand filtration.

Iron, manganese (and aluminium) are leached from soils, particularly by acidic waters, and are present in solution or as complexes with organic material in the water. Aluminium and iron can be precipitated and removed under the same conditions required for colour removal by chemical coagulation. Manganese remains soluble under these conditions. Effective precipitation of manganese can be brought about by a combination of increased pH and addition of an oxidising agent (usually chlorine). The precipitate can then be removed by filtration. Therefore, at least two stages of treatment, and in many cases three stages, each at a different pH, may be required for effective removal of these metals.

Organic micropollutants, i.e. those of concern at very low concentrations, include not only those of anthropogenic origin, such as pesticides and solvents, but also those produced naturally such as taste and odour producing compounds or toxins from algal growth in reservoirs. Activated carbon adsorption or degradation using ozone are used to remove these.

One of the most active areas of development in water treatment over the past 10 years has been in membrane processes, which cover a range of applications from removal of particulates to desalination.

Mechanisms of action for the removal of pesticide compounds by generic processes used in water treatment for types are reviewed below, including the measures and parameters that are used to predict or evaluate performance. This information is provided for background in relation to subsequent information specific to glyphosate and AMPA.

2.2   **Chemical coagulation**

Chemical coagulation may provide limited removal of some organic micropollutants through adsorption on to floc or where they adsorbed on to particulates which are removed by coagulation. The extent of adsorption on to floc or particulates will depend to some extent on the same properties that influence adsorption by activated carbon, as discussed in Section 2.4. It will also depend on the floc or particulate concentrations in the water, in relation to surface area available for adsorption, and on the nature of the floc and particulates. For the majority of organic micropollutants, chemical coagulation will not provide significant removal.

2.3   **Oxidation**

Of the oxidants commonly used in water treatment across Europe, ozone is the most effective for degradation of the majority of organic micropollutants, but some degradation can be achieved using chlorine, chlorine dioxide or potassium permanganate. Ozone is the only oxidant commonly installed specifically for degradation of organic micropollutants. The relative performance of ozone (and other oxidants) for degradation of organics is usually expressed in terms of the first order rate constant. Published examples are given in Table 2.1 for a range of organic micropollutants of common concern in water supply.

The algal toxin microcystin LR is very readily oxidised by ozone, whereas geosmin (a natural compound causing taste and odour problems) is poorly removed. Rate constants may be available for other oxidants used in water treatment, and examples are given in Table 2.2 for microcystin LR, to illustrate the relative magnitude of the rate constant ($M^{-1}s^{-1}$) and the time taken to provide breakdown, given as the half life at an oxidant concentration of 1 mg l^{-1} (at 20°C and pH 7).

Table 2.1   Examples of first order rate constants for micropollutant degradation using ozone

Micropollutant	Rate constant
Microcystin LR[1]	4.1 x 10^5 $M^{-1}s^{-1}$
MCPP[2]	44 $M^{-1}s^{-1}$
Atrazine[2]	12.2 $M^{-1}s^{-1}$
Geosmin[3]	< 1 $M^{-1}s^{-1}$

[1]EU TOXIC programme (2006)
[2]Xiong and Graham (1992).
[3]von Gunten (2003)

Table 2.2   Examples of oxidation kinetics for microcystin LR

Oxidant	Rate constant and half life
Chlorine dioxide	1.1 (12 h)
Potassium permanganate	348 (5 min)
Ozone	4 x 10^5 (0.1 s)
HOCl	90 (10 min)
Monochloramine	0.012 (30 d)

Source: EU TOXIC programme (2006)

The values in Table 2.1 relate to oxidation by molecular ozone, but in water treatment the degradation is often through the generation of hydroxyl radicals, which can be much more effective than molecular ozone for some organic micropollutants e.g. geosmin, and play a more significant role in breakdown despite being at very much lower concentrations. The hydroxyl radical reactions are promoted by higher pH and by the presence of natural organics in the water. However, hydroxyl radical reactions occur less at higher alkalinity, because bicarbonate acts as a scavenger of the radicals.

Hydroxyl radical formation is promoted in "advanced oxidation" processes though the use of hydrogen peroxide in combination with ozone or ultraviolet (UV) irradiation. Effectiveness of this has been demonstrated for a range of organic micropollutants, and benefits can be derived in relation to lower formation of ozonation by-products, particularly bromate.

2.4   Adsorption by activated carbon

The most common adsorbent used in water treatment is activated carbon, used in a granular or powdered form (GAC or PAC). GAC is used in fixed bed adsorbers, and is regenerated when the adsorption capacity is reached, typically every 1-2 years, although this depends on the quality of the water being treated, and longer bed life is possible. PAC is dosed to the

water, and then needs to be removed by subsequent treatment processes such as clarification and filtration.

The efficiency of adsorption for organic micropollutants is dependent upon the physical and chemical properties of the compound, particularly the solubility in water and the octanol:water partition coefficient, usually expressed as the logarithmic value (log K_{ow}). Values of these for pesticide compounds known to be effectively adsorbed by activated carbon under water treatment conditions are shown in Table 2.3.

Table 2.3   Solubility and log K_{ow} values for pesticides adsorbed by activated carbon

Compound	Log K_{ow}	Water solubility (mg l^{-1}) at 20°C
Chlortoluron	2.5	74
Isoproturon	2.5	70
Atrazine	2.7	35
Simazine	2.3	5

Source: EU Footprint database (www.herts.ac.uk/aeru/footprint/)

Better adsorption by activated carbon would be expected for compounds with higher log K_{ow} and lower solubility, although there are exceptions, and this does not always provide a reliable estimate of activated carbon performance.

Laboratory evaluation of activated carbon is carried out using batch isotherm tests which can be used to find the Freundlich isotherm constants (K_f) and 1/n. These values can be used directly to compare the performance of GACs. Values for the Freundlich constants are highly dependant upon the nature of the test water, as well as the type of activated carbon and organic compound. The background concentration of natural organics can strongly influence the extent of adsorption, with much higher adsorption in organics free water (e.g. distilled or deionised) compared with natural raw water or tap water. Published examples of Freundlich constants for organic micropollutants are shown in Table 2.4. The tests for these data used Chemviron F400, a commonly used GAC. Higher values for the Freundlich constants reflect more effective adsorption and removal.

Table 2.4   Examples of Freundlich constants

Compound	K_f (($\mu g.g^{-1}$)(L.(μg^{-1})$^{1/n}$)	1/n	Water type
Atrazine	38,700	0.291	Distilled-deionised
Atrazine	25,100	0.356	Filtered groundwater
Carbofuran	16,400	0.408	Distilled-deionised
Carbofuran	13,100	0.355	Filtered river water

Source: Speth and Miller (1990)

Another parameter used to compare the performance of GAC is the effective carbon dose (ECD), which is the mass of GAC per unit volume treated to a defined breakthrough concentration for a specified organic compound. For example, if a bed containing 10 tonnes of GAC treats 500 Ml to a breakthrough of 0.1 μg l^{-1}, the ECD is 20 mg l^{-1} (i.e. 10,000 kg per 500,000 m^3 = 20 mg l^{-1}). Values for specific throughput are sometimes given, which is the reciprocal of the ECD, usually quoted in m^3 kg^{-1}. An ECD of 20 mg l^{-1} would therefore be a specific throughput of 50 m^3 kg^{-1}. To put this into perspective, a GAC bed operating with an

empty bed contact time (EBCT) of 15 minutes would, if operated for 1 year to specified breakthrough concentration, have treated 35,040 bed volumes, or 35,040 m^3 water per m^3 GAC. Assuming a bulk density of 0.5 for the GAC, this represents 70,080 m^3 per tonne GAC, or a specific throughput of 70.08 m^3 kg^{-1}. The ECD would be 14 mg l^{-1}.

Generally, organic compounds that are amenable to adsorption by activated carbon can be removed by either GAC or PAC. However, PAC is normally used on a temporary basis to deal with short-term seasonal contaminants, such as algal toxins. If activated carbon is needed for more than about 3-4 months per years, it is usually more cost-effective to use GAC, despite high installation costs compared with PAC.

2.5   **Membrane processes**

Of the membrane processes used in water treatment, significant removal of dissolved micropollutants might be achieved through the less commonly used processes of reverse osmosis (RO) or nanofiltration (NF), depending on their molecular weight. In Europe generally, the more commonly used membrane processes are microfiltration (MF) and ultrafiltration (UF), particularly in relation to removal of Cryptosporidium. MF is essentially a particle removal process and would provide no significant removal of most organic micropollutants. UF can remove high molecular weight organics, but would not normally remove most organic micropollutants, which tend to be of relatively low molecular weight compared with natural organics.

All membrane processes would achieve removal of organic micropollutants where they are adsorbed on to particulates.

2.6   **Biodegradation**

Three types of water treatment process, bank infiltration, slow sand filtration (SSF) and biological activated carbon (BAC), rely on biodegradation for removal of organics.

Bank infiltration involves passage of water from rivers or lakes through the ground to intake wells of the water treatment works. Removal of organic micropollutants will depend on the time of travel and adsorption on to the soil, as well as the inherent biodegradability of the compound. Bank infiltration will also remove particulate material from the water, together with any adsorbed compounds. Although widely used in other European countries (including dune infiltration in the Netherlands), this process is not used to any significant extent in the UK.

The majority of biological activity in SSFs occurs in the top few centimetres of the sand, and retention time in this layer is relatively short. Removal therefore depends heavily on adsorption within this layer. As for bank filtration, removal of particulates with adsorbed compounds also occurs.

High concentrations of adsorbed organics together with large surface areas for microbial growth lead to all GAC adsorbers developing biological activity. This is sometimes enhanced by the use of ozone prior to the GAC, which increases the biodegradability of natural organics and encourages microbial growth. This biological activity may sometimes enhance removal of adsorbed compounds which are not normally considered to be particularly biodegradable, such as some pesticides.

2.7 <u>Air stripping</u>

Some organic compounds, particularly the volatile organics such as solvent contaminants in groundwater, can be removed by air stripping, in which the water flows downwards through a packed bed, with forced upflow of air from blowers. The amenability to removal by air stripping for a particular compound is related to it Henry's Constant, which is effectively the equilibrium ratio of the compound in the air phase and liquid phase in a sealed system. The units of Henry's Constant can vary and examples are shown in Table 2.5 for a range of compound and air stripping effectiveness. This process is not generally applicable to pesticide removal, but could contribute to removal depending on the volatility of the compound.

Table 2.5   Examples of Henry's law constants (20°C)

	Atm	Dimensionless	Pa m^3 M^{-1}	Effectiveness of air-stripping
Ammonia	0.79[1]	0.0006	1.4	Poor
Carbon dioxide	151[2]	0.113	277	
Chloroform	170[2]	0.127	311	
Trichloroethene	550[2]	0.410	1,008	↓
Carbon tetrachloride	1,290[2]	0.963	2,363	Excellent

1.   Perry and Green (Eds)
2.   Pontius (Ed) (1990)

3. REMOVAL OF GLYPHOSATE BY WATER TREATMENT

3.1 Introduction

Glyphosate is a broad spectrum, non-selective herbicide, widely used for the post-emergence control of annual and perennial weeds in a variety of agricultural and non-crop applications. EC Directive 98/83 (1998) related to the quality of water for human consumption has set a limit of 0.1 µg l^{-1} for pesticides, their relevant metabolites, decay and reaction products.

The removal capacity of commonly used processes for water treatment for glyphosate and its metabolite AMPA are significant. In this section, a review of the literature summarises the available information regarding the removal of glyphosate and AMPA during various drinking water treatment processes. Although AMPA is regarded as a non-relevant metabolite of glyphosate, the data concerning this compound have been included for completeness.

3.2 Literature Review

3.2.1 Bank and dune infiltration

Whilst not strictly a treatment process, abstraction of surface water through a natural terrestrial matrix and mixing with groundwater, such as occurs with bank and dune infiltration, has been found to remove a proportion of both glyphosate and AMPA.

Lange and Post (2000) studied the occurrence of glyphosate and AMPA in water abstracted from the iver Main at Eddersheim in Germany. The measurements (Table 3.1) show a progressive reduction in AMPA with increasing distance between abstraction and the river. The concentration of glyphosate in the source and abstracted water was less than the limit of detection (0.05 µg l^{-1}).

Table 3.1   Concentration of AMPA in water subject to bank infiltration (Lange and Post, 2000)

Distance from River Main (m)	Abstraction Depth (m)	AMPA (µg l^{-1})
0	0	0.34
70	7	0.26
190	19.5	0.06
530	10.5	< 0.05

Other studies (Hopman *et al.*, 1995; Schlett *et al.*, 2005) also indicate removal of AMPA by infiltration, but concurrent concentration measurements for glyphosate were too small to draw conclusions.

It is well known that glyphosate readily adsorbs to soil and is degraded, so that removal by infiltration would be expected. The extent to which this occurs will depend on the time of passage of the water, and the properties of the soil.

A Dutch study (IJpelar *et al.*, 2000) reported concentrations of up to 0.49 μg l^{-1} glyphosate and 5.4 μg l^{-1} AMPA in surface waters. Bank and dune filtration reduced AMPA by between 40% and >90% at a range of sites; corresponding data for glyphosate were not provided.

3.2.2 Chemical coagulation and clarification / filtration

The removal efficiency of glyphosate and AMPA by chemical coagulation based treatment processes appears to be highly variable, ranging from less than 10% to over 80% depending on the type of coagulant, pH and solids-liquid separation process used. Removal is reported to be more efficient when floc separation is achieved by filtration rather than flotation, and this would be consistent with adsorption of the compounds on to particulates (including floc particles), and subsequently more efficient particulate removal occurring by filtration compared with flotation.

Speth (1993) reported very poor removal of glyphosate by coagulation with aluminium sulphate, followed by rapid filtration. However, it should be noted that the turbidity of the filtered water was relatively high (2 NTU), suggesting non-optimal conditions of coagulant dose and/or pH, which may well have biased the results.

Hopman *et al.* (1995) evaluated different coagulants (ferric chloride, ferrous sulphate, aluminium sulphate and polyaluminium chloride) at four locations in the Netherlands. The concentration of AMPA in the raw water (0.26 – 0.88 μg l^{-1}) was reduced at 3 out of 4 of the sites by 49% to 83%. At the fourth site there was little or no removal, possibly due to the floc separation process (upflow filtration). Removal of glyphosate was less easily assessed, due to very low initial concentrations, often below the limit of detection.

Kempeneers (2000) studied the removal of glyphosate and AMPA, using an aluminium based coagulant to treat a spiked surface water, derived from the River Meuse. The results (Table 3.2) indicated a wide range of removal efficiency for both glyphosate and AMPA, with initial concentrations of 1 and 5 μg l^{-1} for glyphosate and AMPA respectively. Dual layer filtration was generally more efficient than flotation, as would be expected in terms of solids removal efficiency.

Table 3.2   Glyphosate and AMPA removal efficiency by coagulation and floc separation processes (Kempeneers, 2000)

Treatment process (pilot scale)	Glyphosate (% removed)	AMPA (% removed)
Coagulation + Flotation	6 – 31 (mean 16)	10 – 57 (mean 19)
Coagulation + Dual layer filtration	15 – 58 (mean 40)	12 – 88 (mean 26)

Monitoring at the Main water treatment works in Germany (Lange and Post, 2000) indicated that the raw water concentration (0.1 µg l^{-1} glyphosate and 0.32 µg l^{-1} AMPA) was reduced by coagulation and flocculation by 39 ± 14 % for glyphosate and 22 ± 15% for AMPA.

At full scale treatment works Ijpelaar *et al.* (2000) reported approximately 90% reduction of AMPA by coagulation / clarification, for an influent concentration of 1.8 - 3.3 µg l^{-1}. Jar tests were used to investigate the effect of pH and coagulant type. The removal efficiency of AMPA was found to be strongly related to pH, decreasing significantly at pH > 7 for an iron based coagulant. The aluminium coagulant was markedly less efficient than the iron coagulant at a single pH (7.1). However tests with a full matrix of dose and pH would be required to fully investigate this comparison.

Roche *et al.* (2004) studied the removal of glyphosate and AMPA by coagulation, using a surface water spiked with a range of contaminants including glyphosate (1 µg l^{-1}). Either aluminium polychlorosulphate (WAC HB, 30 mg l^{-1}) or ferric chloride (FeCl$_3$, 30 – 70 mg l^{-1}) were used as coagulants, with suitable pH adjustment. The results are shown in Table 3.3.

Table 3.3   Removal of glyphosate and AMPA by coagulation as a function of pH and flocculation type (Roche *et al.*, 2004)

	Glyphosate				AMPA			
pH	5	6	7	8	5	6	7	8
Removal using WAC	34%	69%	43%	45%	20%	40%	<15%	15%
Removal using FeCl$_3$	88%	87%	84%	47%	67%	70%	47%	<15%

The performance of coagulation for incorporation of particulates from the water and the formation of stable floc particles is strongly dependant upon pH and coagulant concentration, and is also influenced by the type of coagulant used for a particular water source. Apparent differences between coagulants will therefore arise because of the suitability of the type of coagulant for a specific water source, rather than a fundamental characteristic of the coagulant in relation to glyphosate and AMPA. Adsorption of glyphosate and AMPA on to particles and floc will also be pH dependent. The range of effects reported in the literature is therefore not unexpected, given the variation in test conditions.

3.2.3   Slow sand filtration

Limited amounts of data available for slow sand filtration indicate a range of performance for removal of glyphosate and AMPA, from 25% to over 75%. Some removal would be expected through adsorption, biodegradation and removal of particulates, but this could be highly dependent upon operating conditions and general performance of the filter for particulate removal. The time since the filter was last cleaned could be a significant factor, particularly in relation to biodegradation and particulate removal. Water temperature will also have a significant influence in relation to biodegradation.

Hopman *et al.* (1995) evaluated the removal of glyphosate and AMPA in slow sand filters at two locations (Scheveningen and Leiduin). For five measurements, glyphosate was not detected in the influent or effluent; AMPA was reduced from concentrations up to a maximum of 0.48 µg l^{-1}, to <0.05 µg l^{-1} (>80% removal).

Schlett (2005) studied the effect of slow sand filtration at a treatment works on the River Ruhr at Styrum-Ost. The inlet water contained <0.05 µg l^{-1} to 0.19 µg l^{-1} glyphosate, reducing to <0.08 µg l^{-1} after filtration. The concentration of AMPA was in the range <0.08 - 0.7 µg l^{-1} at the inlet, and was reduced to <0.08 µg l^{-1} after filtration.

3.2.4   Chlorination

The literature suggests that chlorine is highly effective in reducing the concentration of glyphosate and AMPA at the concentrations and contact time used in water treatment. Hopman *et al.* (1995) noted that the 'degradation' of AMPA was not due to oxidation, but involved the *addition* of chlorine to the AMPA molecule. Hopman's work referred to 'transport chlorination', which relates to the use of chlorine in the distribution system. Contact times were not given, but were presumably in excess of 24 hours.

The performance of chlorine will be temperature and pH dependant, but little information related to the impact of these factors was found.

Speth (1993) carried out pilot scale tests with Ohio river water spiked with a very high glyphosate concentration of 739 µg l^{-1}. With an applied chlorine dose of 2.1 mg l^{-1}, the glyphosate concentration was reduced below the limit of detection (25 µg l^{-1}) after 7.5 minutes contact. Temperature and pH conditions were not described.

Hopman *et al.* (1995) found that when chlorine was dosed for distribution chlorination (0.2 – 0.6 mg l^{-1} chlorine), between 40 - 100% of AMPA was removed for initial concentrations of 0.2 - 5 µg l^{-1}. A chlorine dose of 2 mg l^{-1} removed >98% AMPA. Contact times were not stated, but are presumed to be relatively long for distribution purposes.

Kempeneers (2000) carried out extensive tests on the removal of AMPA and glyphosate with chlorine. In the first series of tests, 1.2 µg l^{-1} glyphosate was found to be completely removed by a chlorine dose of 2 mg l^{-1}, after a contact time of 20 minutes, and 0.56 µg l^{-1} AMPA was removed for the same conditions. A concentration of 5 µg l^{-1} glyphosate was removed by a chlorine dose of 0.75 mg l^{-1}, after a contact time of 4 hours, and 0.42 µg l^{-1} AMPA was removed under the same conditions.

Further experiments, with much shorter contact times were used. After a contact time of 120 seconds, 11.5 µg l^{-1} glyphosate and 0.14 µg l^{-1} AMPA were completely removed, indicating extremely fast kinetics.

Lange and Post (2000) found that a chlorine concentration of 0.08 mg l^{-1} Cl_2 achieved 74 and 80% removal of glyphosate and AMPA respectively, for a drinking water spiked at 0.05 – 0.4 µg l^{-1}, after a contact time of 5 minutes. A higher (more typical) chlorine dose of 0.40 mg.l^{-1} achieved 94% removal.

A summary of the removals of glyphosate and AMPA by chlorine is shown in Table 3.4 and 3.5. The 'greater than' values in the table reflect the limit of detection for the glyphosate analysis. Generally, removal is above 95% except for the Lange and Post tests where the

removal (74%) was probably limited by an unrealistically low chlorine dose and short contact time, and/or limitations in the analysis and calculation due to glyphosate concentrations close to the detection limit.

Table 3.4   Removal of glyphosate by chlorine

	Chlorine applied (mg l^{-1})	Contact time (minutes)	Initial glyphosate concn. (µg l^{-1})	% removal glyphosate
Kempeneers (2000)	2.00	20	1.2	> 95
	0.75	240	5	> 99
	0.75	2	11.5	> 99
Lange / Post (2000)	0.08	5	0.05 – 0.4	74
	0.40	5	0.05 – 0.4	94
Speth (1993)	2.10	7.5	739	> 96

Table 3.5   Removal of AMPA by chlorine

	Chlorine applied (mg l^{-1})	Contact time (minutes)	Initial AMPA concn. (µg l^{-1})	% removal AMPA
Kempeneers (2000)	2.00	20	0.56	> 90
	0.75	240	0.42	> 88
	0.75	2	0.14	> 65
Lange / Post (2000)	0.08	5	0.05 – 0.4	80
	0.40	5	0.05 – 0.4	95
Hopman (1995)	2.00	-	0.63 – 0.74	> 95
	0.20 – 0.60	-	0.2 – 5.0	40 - 100

The impact of chlorination on glyphosate residues in drinking water has further been evaluated by using isotope labelled glyphosate, allowing direct analysis and detection of intermediates (Brosillon, 2006 and Mehrsheikh, 2006). The following degradation pathways were identified:

- Carboxylic acid carbon of glyphosate/glycine is converted to CO_2;

- C2 of glyphosate/glycine is converted to CO_2 and methanediol;

- C3 of glyphosate is converted to methanediol;

- Nitrogen atom of glyphosate/glycine is transformed to nitrogen and nitrate;

- Phosphorus atom of glyphosate is converted to phosphoric acid;

- The terminal glyphosate chlorination products are not unique to glyphosate and are also formed from chlorination of other natural organic matter present in water.

These chlorination by-products were formed over a 24 hour period, at pH 7 and 8, at a range of chlorine to glyphosate ratios. Glyphosate decay was complete at molar ratios of 2 or greater. Further tests, using purified water at chlorine to glyphosate ratios of up to 4, found that the reaction was very fast, with complete removal when the first sample was taken after 10 minutes. Modelled results indicated 99% removal after 5 seconds.

3.2.5   Chlorine dioxide

Despite being generally considered as at least as strong an oxidising agent as chlorine, a limited amount of data in the literature suggests that chlorine dioxide is much less effective in removal of glyphosate.

Speth (1993) reported a pilot scale treatment system which included dosing chlorine dioxide prior to coagulant dosing. The initial concentration of glyphosate (739 μg l^{-1}) was unrealistically high. A residual of 1.07 mg l^{-1} Cl_2 was measured after coagulation with aluminium sulphate, and the combined effect of chlorine dioxide and coagulation was a reduction of glyphosate to 590 μg l^{-1}. After sedimentation (9h contact time), the ClO_2 residual had reduced to 0.26 mg l^{-1} and glyphosate had reduced to 329 μg l^{-1}, achieving an overall reduction of 56%.

3.2.6   Ozone

The work reported in the literature suggests that better than 90% removal of glyphosate and AMPA can be achieved with ozonation. Less removal of AMPA was seen for some tests, although it was not possible to identify the reasons for this from the information provided. It is possible that the water used in some of these tests had a high ozone demand, such that the ozone concentration available for degradation of glyphosate / AMPA was small.

Klinger *et al.* (2000) carried out tests with deionised water, which resulted in poor removal of both glyphosate and AMPA. This may have been due to a low concentration of free radicals, particularly as removal was greater at increased pH (see Section 2.3).

Yao and Haag (1991) derived the following expression for estimating the reaction rate constant for glyphosate with ozone for pH 6 to 9:

$$k \approx \frac{0.005[H^+] + 5.5 \times 10^{-10}}{[H^+]^2 + 1.3 \times 10^{-6}[H^+]}$$

where:
k = reaction rate constant, M^{-1}s^{-1} (comparable with the values discussed in Section 2..3)
[H$^+$] = hydrogen ion concentration

Making the simplifying assumption that

$$[H^+] = 10^{-pH}$$

then approximate values of k are as shown in Table 3.6. The calculated half-lives (t½) for an ozone concentration of 1 mg l^{-1} are also shown. These confirm that ozone is highly effective for glyphosate degradation, with increasing efficiency at higher pH.

Table 3.6 **Estimates of reaction rate constants (k) and half-life (t½) (for ozone concentration = 1 mg l^{-1}) for glyphosate (Yao and Haag, 1991)**

pH	6	7	8	9
k, M[-1]s[-1]	2400	7500	45800	427000
t½ (seconds)	14	4.4	0.7	0.08

Because of the experimental approach taken by Yao and Haag, the derived values of k are over-stated by a factor of η, where η represents the reaction stoichiometry:

1 mole ozone + η moles glyphosate $\rightarrow$ reaction products

Yao and Haag (1991) did not provide a value of η, but did state that values in the range 1 to 4 are typical for reactions with organic compounds. From Table 3.6, the practical implications of a value of factor of η = 4 are not great in the context of typical ozone dose and contact time. Even at pH 6, a half-life of 56 seconds (i.e. 14 x 4 seconds) is much shorter than typical full scale contact times of at least 10 minutes, and, allowing for this correction for the approach taken, the effectiveness of ozone for glyphosate removal is still apparent. The tests from which the rate constants were derived were carried out at a relatively high water temperature of 20-25°C. At lower temperature the rates would be lower, but the practical significance is unlikely to be great in terms of the overall performance of ozone.

In pilot plant tests Speth (1993) reported that a dose of 1 mg l^{-1} ozone removed only 60% of glyphosate after 7 minutes contact time. Increased ozone doses of 1.9 mg l^{-1} and 2.9 mg l^{-1}, more typical of those used in water treatment, gave complete removal of the very high initial concentration of glyphosate (800 - 1000 μg l^{-1}). The ozone demand of the water (including the contribution from the high glyphosate concentration) probably made insufficient ozone available to provide effective glyphosate removal at the lowest ozone dose.

Hopman (1995) reported a large variation in ozone performance relating to full scale treatment in the Netherlands, at 4 sites. Glyphosate was only detected once in the inlet water at one site, where a dose of 0.8 mg l^{-1} ozone reduced 22 μg l^{-1} glyphosate to below the limit of detection. AMPA was more prevalent, 7 out of 10 measurements showed between 25 and 77% reduction of AMPA; the remaining 3 measurements indicated an increase in AMPA after ozonation, suggesting production of AMPA from breakdown of glyphosate, without further degradation. The extent to which this would occur is likely to be a function of ozone dose/concentration and pH, with less potential for AMPA production at higher dose and pH, in relation to concentrations of both ozone and hydroxyl radicals.

Klinger *et al.* (1998) found that it was possible to generate glyphosate and AMPA by ozonation of water (at pH 5) containing EDTMP (methylenephosphonic acid) which is a complexing/chelating agent used in many industrial processes and may occur in river water in industrial areas. The implication is that a proportion of glyphosate and AMPA measured in ozonated water is not herbicide derived. However, the practical implications of this for public water supplies is uncertain.

In a laboratory study, Roche *et al*. (2004) applied ozone at 1, 2 and 3 mg l^{-1} using water with dissolved organic carbon concentration of 0.6 and 2.0 mg l^{-1}, spiked with 1.1 and 1.8 µg l^{-1} of both AMPA and glyphosate. Ozonation with 10 minutes contact time resulted in a reduction of >94% and 90% of glyphosate and AMPA respectively. Actual effective doses were calculated as significantly less than described, due to transfer inefficiency, and therefore the performance of ozonation was better than implied by the applied ozone doses.

Generally, the results suggest that ozonation as applied in water treatment is highly effective for degradation of both glyphosate and AMPA, and that the mechanism involves hydroxyl radicals rather than free ozone. A summary of the results from the literature are shown in Table 3.7.

Table 3.7   Summary of effects of ozone on glyphosate and AMPA

	Glyphosate (µg l^{-1})	AMPA (µg l^{-1})	O_3 applied (mg l^{-1})	Contact time (min.)	% removal glyphosate	% removal AMPA
Roche (2004)*	1.8	1.1	1	10	>94	> 90
	1.8	1.1	2	10	>94	> 90
	1.8	1.1	3	10	>94	> 90
Klinger (2000)**	1000	1000	3	10	>99	95
Speth (1993)***	800^{-1}000	-	1.0	7	60	-
	800^{-1}000	-	1.9	7	>97	-
	800^{-1}000	-	2.9	5.3	>97	-
Hopman (1995) °	22 (n = 1)	0.1 – 0.62 (n = 7)	0.8 - 2	-	>95	25 - 77

*: pretreated water; ** bank filtrate; *** surface water, ° different waters

3.2.7   UV and advanced oxidation

No references to use of UV or advanced oxidation processes were found relating to removal of glyphosate or AMPA. However, the significance of the hydroxyl radical reactions for breakdown of glyphosate and AMPA (Section 3.6) would imply that ozone/peroxide or UV/peroxide processes would be effective.

3.2.8   Activated carbon

Glyphosate is reported to have a log K_{ow} in the range -3.2 (at 25 °C, pH 5-9) to -1. This indicates high water solubility and an expectation of very limited adsorption by activated carbon. The compounds may be more amenable to removal through the development of biological activity in GAC (BAC), although the mechanism may depend strongly on adsorption of the compounds first to allow effective biodegradation.

Freundlich constants are provided by Speth (1993) for tests carried out in distilled water:

K_f = 96,100 (µg g^{-1})(L (µg^{-1})$^{1/n}$

1/n = 0.062

This K_f value is high compared with values given for atrazine which is amenable to adsorption by activated carbon, suggesting GAC would be effective for glyphosate. However, Speth also reports results for tests carried out in river water, which show very much lower Freundlich constants, consistent with the relatively poor removal seen in other work. The presence of competing natural organic matter would be expected to reduce the capacity of the GAC to adsorb glyphosate or AMPA.

Lange and Post (2000) reported an average removal of 21% of AMPA by GAC, for a pretreated surface water (coagulation and rapid gravity filtration) but less than 10% removal for Glyphosate. The results for AMPA show removal decreasing very quickly to less than 40% after a specific throughput of 2 m^3 kg^{-1} and less than 20% after a specific throughput of 9 m^3 kg^{-1}. This represents effective operation for only a week or two, despite low influent concentrations of 0.06 μg l^{-1} Glyphosate and 0.25 μg l^{-1} AMPA.

Hopman *et al.* (1995) found that at one site in the Netherlands, GAC with a run time of 75,000 bed volumes (22 months operation) reduced an AMPA influent concentration of 0.33 μg l^{-1} to 0.04 μg l^{-1}. At other sites in the same study, the mean removal was 69%.

Kempeneers (2000) reported a mean of 97% removal of glyphosate and 60% AMPA for experimental evaluations, using virgin GAC and a spiked concentration of 1 μg l^{-1}. The removal only lasted a few days and would not offer any practical benefit for use of GAC. However, it may mean that powdered activated carbon (PAC) could be more effective, as it is always dosed as a virgin material. However, there appears to be no information available on the use of PAC for glyphosate or AMPA.

3.2.9 Pressure driven membrane processes

Laboratory scale tests (Roche *et al.*, 2004) with nanofiltration were carried out on a group of seven pesticides, including AMPA and glyphosate. Distilled water spiked with 2 μg l^{-1} AMPA and glyphosate and 500 mg l^{-1} $CaCl_2$ (pH 7, temperature: 25°C) was tested at a flux of 20 liters/hour/m^2. The retention (i.e. removal) of glyphosate and AMPA was > 95% after 72 hours.

Hopman *et al.* (1995) tested 4 low pressure "hyper filtration" (RO) membranes in a pilot plant and were able to reduce glyphosate concentrations of 4.5 μg l^{-1} to below the detection limit.

Speth (1993) evaluated the removal of glyphosate through ultrafiltration membranes with a molecular weight cut-off (MWC) of 100,000; 1,000 and 500. The experiments, carried out at bench scale, showed that glyphosate was not removed from surface water by 100,000 MWC membranes even when the turbidity was below 0.2 NTU. The 1000 MWC membranes initially rejected 50% of the glyphosate and the 500 MWC membranes initially removed all glyphosate.

Whilst nanofiltration and RO have been shown to remove glyphosate and AMPA, large scale production of water by these methods is very expensive, not commonly used and unlikely to be adopted for removal of organic micropollutants. Some removal by ultrafiltration is possible, depending on the membrane type, but the low molecular weight cut-off membranes, reported to give good removal, are little used in practice for large scale water treatment because of high operating costs.

A summary of the removal of glyphosate and AMPA by membrane filtration is given in Table 3.8.

Table 3.8   Summary of removal of glyphosate and AMPA by membrane filtration

	Membrane	**Water type**	**Glyphosate Added**	**AMPA added**	**Glyphosate removed**	**AMPA removed**
Roche (2004)	NF 90 (DOW)	Distilled water	2 µg l^{-1}	2 µg l^{-1}	> 95%	>95%
Speth (1993)	AMICON UF	Ohio River water	350 µg l^{-1}	-	50 - 100 %	-
Hopman (1995)	RO	Groundwater	4.5 µg l^{-1}	-	> 90%	-

3.2.10   Air stripping

The Henry's Law Constant for glyphosate (2.1 x 10^{-7} Pa m^3 M$^{-1)}$, in comparison with values for other compounds given in Table 2.5, indicate that it would not be amenable to removal by air stripping.

3.2.11   Summary of removal of glyphosate and AMPA by water treatment processes

Bank and dune filtration

Physical removal of particulates, adsorption on to soils and biological degradation enable bank and dune filtration to remove a proportion of glyphosate (17 - 45% reported) and AMPA (65% reported). This will be dependent upon the retention time and water temperature, as well as the soil properties.

Conventional physico-chemical processes

Coagulation followed by solid-liquid separation (clarification by flotation or sedimentation) and rapid gravity filtration, can remove a proportion of both glyphosate and AMPA, but is unlikely to provide a reliable effective barrier in all situations. Removal will depend on the extent of adsorption of the compounds on to particulates and floc, and the degree of particulate/floc removal by solids-liquid separation processes. The wide range of performance reported in the literature probably reflects the importance of optimising the coagulation process (coagulant dose and pH) as well as 'real world' variation in clarifier performance.

Slow sand filtration

There is insufficient information in the literature to predict performance of slow sand filtration with respect to removal of glyphosate or AMPA. However, it is likely that removal would be

less effective than bank or dune filtration, because similar mechanisms are involved but retention times in slow sand filtration are very much lower (hours rather than several days).

Chlorine

Application of chlorine at doses typical of disinfection of surface waters, is capable of very effective degradation of glyphosate. Lower degradation of AMPA is expected, but chlorination still provides an effective barrier. Because of the importance of temperature and pH to chlorination chemistry, it would be valuable to investigate the impact of these factors on degradation of glyphosate and AMPA.

Chlorine dioxide

The use of chlorine dioxide for this application is not widely reported, and no clear conclusions can be drawn. However, based on limited data, chlorine dioxide would not appear to be effective for glyphosate removal.

Ozone

Ozonation is capable of very effective degradation of glyphosate and AMPA. The mechanism for breakdown of glyphosate and AMPA by ozone appears to rely on free radical generation, and would be more effective at higher pH. There are indications that, in some circumstances, AMPA may increase in concentration after ozonation or AMPA removal may appear to be less efficient, possibly as a result of breakdown of glyphosate to produce AMPA by ozonation.

UV and advanced oxidation

The use of UV alone is not documented for this application, and no conclusions can be drawn. UV would not be expected to be effective at doses typically used in water treatment, but may be effective at very high doses. Advanced oxidation techniques, including combined UV/H_2O_2 or ozone with H_2O_2, have significant potential through free radical mechanisms, but no reported information was found for removal of glyphosate and AMPA.

Activated carbon

GAC is likely to be of limited use for the removal of glyphosate or AMPA. Removal may be effective with virgin or freshly regenerated GAC, but only for a short period. Selection of carbon type, contact time, and possibly pH may help to improve removal, but it is unlikely to provide a reliable barrier for meeting a target of <0.1 μg l^{-1}.

No information was available on the performance of PAC for glyphosate and AMPA. Because virgin GAC appears to be effective for a short period, it is possible that PAC would be more effective than GAC. It would be valuable to investigate this further through laboratory tests. Use of PAC could be considered to deal with seasonal short-term peaks in glyphosate and AMPA in the raw water.

Membrane filtration

Nanofiltration and Reverse Osmosis are capable of effective removal of glyphosate; very limited tests also indicate similarly good removal of AMPA. Ultrafiltration is unlikely to be a suitable process for removal of significant concentrations of glyphosate or AMPA. Partial removal would be expected for all membrane processes where these organic substances are adsorbed on to particulate matter.

Air stripping

The Henry's Law Constant for glyphosate indicate that it would not be amenable to removal by air stripping.

Overall Summary

A summary of the expected removal efficiency of specific, commonly used treatment processes is given in Table 3.9 showing the range of removal found and a summary of practical implications. For chlorination and ozonation, the lower removals are associated with low oxidant doses and contact times compared with those commonly used in water treatment, or limitations due to the detection limits. For other processes, the range of removal will be related to variations in test/process operating conditions.

Table 3.9   Removal of glyphosate and AMPA by treatment processes

Treatment Process	Glyphosate removal (%)	AMPA removal (%)
Bank and dune filtration	20 to 50	25 to 95
Aluminium coagulant and clarification	15 to 40	20 to 25
	Not a reliable barrier for Glyphosate and AMPA	
Iron coagulant and clarification	40 to 70	20 to 85
	Not a reliable barrier for Glyphosate and AMPA	
Slow sand filtration	Insufficient information but likely to be less effective than bank or dune filtration and therefore of little practical benefit	
Chlorination	74 to > 99	40 to >95
	Likely to provide the main barrier to Glyphosate and AMPA at most water treatment works	
Chlorine dioxide	Insufficient information but not expected to be effective	
Ozonation	60 to >99	25 to 95
	Provides an additional barrier at works where already installed for other pesticides and micropollutants	
UV irradiation	No information found. Highly unlikely to be effective alone at doses used in water treatment. May be effective at very high doses not currently used for water treatment.	
Advanced oxidation	No information found, but would be expected to be effective through free radical mechanisms. Little used for water treatment at the present time.	
Activated carbon adsorption	10 to 90	20 to 70
	Higher removals relate to virgin GAC and are unlikely to be achieved under practical conditions. Not a reliable barrier for Glyphosate and AMPA.	
Membrane filtration	>90 (NF/RO) >50 (UF)* *depending on membrane type	>95 (NF/RO) No information found for UF
	Membrane processes not widely used in water treatment, and unlikely to be installed solely as a barrier to pesticides and other organic micropollutants.	
Air stripping	No information found, not expected to be effective based on chemical characteristics.	

4. CONCLUSIONS

The majority of water treatment works worldwide use chlorine for disinfection, and therefore have an effective barrier for glyphosate and AMPA. Exceptions to this would be works in mainland Europe which use chlorine dioxide for disinfection and protection of the water in distribution, instead of chlorine.

The most common water treatment process installed for removal of pesticides worldwide is adsorption using granular activated carbon. This would not appear to provide an effective barrier to glyphosate and AMPA. However, at many treatment works ozone is also installed for removal of pesticides or other organic micropollutants, and would be highly effective for glyphosate and AMPA removal under the dose and contact time conditions typically used.

Other processes commonly used in water treatment (bankside or dune infiltration, coagulation/clarification/filtration and slow sand filtration) would each contribute some removal, but each process in isolation is unlikely to provide a secure barrier in relation to meeting a 0.1 μg l^{-1} standard.

Chemical coagulation based treatment is the most common water treatment process worldwide. In principle, this may be optimised to maximise removal of glyphosate and AMPA. However, this would not be possible if it conflicted with the optimum conditions for the main objectives of chemical coagulation i.e. removal of natural organic material, colloidal material and particulates. The relationship between pH and coagulant type and dose therefore requires further definition in relation to removal of glyphosate and AMPA, compared to other contaminants.

Examples of performance of typical water treatment process streams are given below, based on the following (probably conservative) assumptions for glyphosate removal:

Bankside/dune infiltration	30%
Chemical coagulation/clarification/filtration	20%
Slow sand filtration	20%
Ozonation	95%
GAC	20%
Chlorination	95%

Based on these expected removal efficiencies, the performance of example combinations of treatment processes are compared in Table 4.1 as the maximum glyphosate concentrations in the raw water reaching the works, to be reduced to less than 0.1 μg l^{-1} in the final treated water.

For example, a treatment works with coagulation, clarification, filtration and chlorination could receive raw water containing 2.5 μg l^{-1}, and still be expected to meet the 0.1 μg l^{-1} (or less) in the final treated water:

- 2.5 μg l^{-1} reduced to 2 μg l^{-1} by chemical coagulation, clarification & filtration (20% reduction);

- 2 μg l^{-1} reduced to 0.1 μg l^{-1} by chlorination (95% reduction).

The values shown in Table 4.1 are only for glyphosate. If there was a need to maintain AMPA below 0.1 μg l^{-1} as well as glyphosate, or to maintain the total (glyphosate + AMPA) below 0.1 μg l^{-1}, the maximum values would relate to the individual concentrations or combined concentrations respectively. This is based on the assumption that removal efficiency of AMPA is similar to that for glyphosate.

Table 4.1   Performance of typical water treatment process streams

Process combination	Glyphosate in raw water to maintain <0.1 μg l^{-1} in the final treated water
Bankside/dune infiltration, slow sand filtration	< 0.18 μg l^{-1}
Bankside/dune infiltration, slow sand filtration, chlorination (or ozonation)	< 3.6 μg l^{-1}
Bankside/dune infiltration, coagulation/clarification/filtration	< 0.18 μg l^{-1}
Bankside/dune infiltration, coagulation/clarification/filtration, chlorination (or ozonation)	< 3.6 μg l^{-1}
Coagulation/clarification/filtration	<0.12 μg l^{-1}
Coagulation/clarification/filtration, chlorination (or ozonation)	< 2.5 μg l^{-1}
Coagulation/clarification/filtration, GAC	<0.16 μg l^{-1}
Coagulation/clarification/filtration, GAC, chlorination (or ozonation)	< 3.1 μg l^{-1}
Coagulation/clarification/filtration, ozonation, GAC, chlorination	< 31 μg l^{-1}

No information was found on the performance of PAC for glyphosate or AMPA removal. Because virgin GAC appears to be effective for a short period, it is possible that PAC would be more effective than GAC. It would be valuable to investigate this further through laboratory tests. Use of PAC could be considered to deal with seasonal short-term peaks in glyphosate and AMPA in the raw water.

Because of the importance of oxidation for glyphosate and AMPA removal, it would also be valuable to investigate the impact of pH and temperature on chlorination performance. Little information was found on this, and chlorination of surface waters during water treatment can occur over a range of temperature from around 2°C to above 20°C, and a pH of between 6 and 9. It would also be valuable to check that ozonation is effective at low water temperature.

Further information on glyphosate removal by water treatment process streams used in the Netherlands is given in Appendix A, based on the same assumptions as given above.

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APPENDIX A   PERFORMANCE OF WATER TREATMENT PROCESS STREAMS IN THE NETHERLANDS

Information on water treatment process streams in the Netherlands is provided in a RIVM report (Wuijts and Van Rijswick, 2007). Table 5.1 of the RIVM report summarises surface water treatment streams in use at Dutch water treatments works. An annotated version of this table is given below to provide estimates of glyphosate for each process stream. Assumptions for removal by individual processes are based on information given in Sections 3 and 4 of this report.

Company	Location	Steps
WHL	Heel	**Infiltration/AIR-cascade/SF/GAC/UV** Assumptions: Infiltration; 30% removal AIR-cascade; no removal SF (assuming no preceding chemical cougulation); no removal GAC; 20% removal UV (assuming for disinfection); no removal *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 0.18 μg l^1*
	Roosteren	**Infiltration/AIR/SF/AIR/UV + GAC as from 2008** *As for Heel*
Evides	Kralingen	**BAS/FCU/SE/O3/SF/GAC/ClO2** Assumptions: BAS; no removal FCU/SE/SF; 20% removal O3; 95% removal GAC; 20% ClO2; 50% *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 6.25 μg l^1*
	Berenplaat	**BAS/MS/FCU/SE/SF/UV/GAC/ClO2** Assumptions: BAS; no removal MS; no removal FCU/SE/SF; 20% removal UV (assuming for disinfection); no removal GAC; 20% ClO2; 50% *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 0.31 μg l^1*

Company	Location	Steps
Evides	Baanhoek	**BAS/FCU/FL/SF/O3/GAC/ClO2** Assumptions: BAS; no removal FCU/FL/SF; 20% removal O3; 95% removal GAC; 20% ClO2; 50% *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 6.25 μg l^1*
	Braakman	**BAS/FCU/FL/O3/SF/GAC/ClO2** Assumptions: BAS; no removal FCU/FL/SF; 20% removal O3; 95% removal GAC; 20% ClO2; 50% *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 6.25 μg l^1*
	Ouddorp	**Preclean= MS/FCU/SF-double layer Infiltration/AIR/SF/GAC/UV** Assumptions: MS/FCU/SF-double layer; 20% removal Infiltration; 30% removal AIR; no removal SF; no removal GAC; 20% removal UV (assuming for disinfection); no removal *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 0.22 μg l^1*
	Haamstede	**Preclean as above Infiltration/AIR/SF/O3/GAC** Assumptions: MS/FCU/SF-double layer; 20% removal Infiltration; 30% removal AIR; no removal SF; no removal O3; 95% removal GAC; 20% removal UV (assuming for disinfection); no removal *Maximum concentration in raw water to maintain <0.1 μg l^1 in final treated water = 4.3 μg l^1*

Company	Location	Steps
DZH	Katwijk	**Preclean in Brakel: FCU/SE/MS/SF** **Dune infiltration/PAC/AIR/DH-pellets/SF/SSF** Assumptions: FCU/SE/MS/SF; 20% removal Infiltration; 30% removal PAC; 20% removal AIR; no removal DH-pellets; no removal SF; no removal SSF; 20% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 0.28 μg l^1*
	Scheveningen	**Preclean in Brakel** **Dune infiltration/DH-pellets/AIR/PAC/SF/SSF** Assumptions: Preclean in Brakel; 20% removal Infiltration; 30% removal DH-pellets; no removal AIR; no removal PAC; 20% removal SF; no removal SSF; 20% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 0.28 μg l^1*
	Monster	**Preclean in Brakel** **Dune infiltration/DH-pellets/AIR/PAC/SF/SSF** *As for Scheveningen*
Vitens	Weerloseweg	Uptake Twentekanaal surface water stopped – quality concerns on microbiological- and micro-pollutants. Extension with membranes in study.
PWN	Andijk	**MS/FCU/FL/SF/UV-H2O2/GAC/ClO2-occasionally** Assumptions: MS; no removal FCU/FL/SF; 20% removal UV-H2O2; 95% removal GAC; 20% removal ClO2; 50% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 6.25 μg l^1*
	Bergen	**Andijk water + infiltration/AIR/SF** Assumptions: Additional removal above that achieved at Andijk. Infiltration; 30% AIR; no removal SF; no removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water:* *at Bergen = 0.14 μg l^1* *at Andjik = 8.7 μg l^1*

Company	Location	Steps
	Mensink	**Andijk water + infiltration/DH/AIR-cascade/SF/ClO2** Assumptions: Additional removal above that achieved at Andijk. Infiltration; 30% DH; no removal AIR-cascade; no removal SF; no removal ClO2; 50% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water:* *at Bergen = 0.29 μg l^1* *at Andjik = 17.9 μg l^1*
	Heemskerk	**UF/RO** Assumption: 99% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 10 μg l^1*
Waternet	Leiduin	**Preclean Nieuwegein: FL/SE Infiltration/O3/DH/SF/GAC/SSF** Assumptions: FL/SE (assuming coagulation also used); 20% Infiltration; 30% O3; 95% removal DH; no removal SF; no removal GAC; 20% removal SSF; 20% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 5.6 μg l^1*
	Weesperkapsel	**BAS/FCU/SE/SF/O3/DH/GAC/SSF** Assumptions: BAS; no removal FCU/SE/SF; 20% removal O3; 95% removal DH; no removal GAC; 20% removal SSF; 20% removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 3.9 μg l^1*
Groningen	DePunt	**BAS/FCU/SE/SF/GAC/AIR/SF/SSF/UV** Assumptions: BAS; no removal FCU/SE/SF; 20% removal GAC; 20% removal AIR; no removal SF; no removal SSF; 20% removal UV (assuming for disinfection); no removal *Maximum concentration in raw water to maintain* *<0.1 μg l^1 in final treated water = 0.2 μg l^1*

Legend :

AIR : aeration
BAS : basin storage
ClO2 : chlorine dioxide
DH : de-hardening (softening)
FCU : flocculation
FL : flotation
GAC : active carbon filtration
H2O2 : peroxide
MS : microsieves
O3 : ozone
PAC : powdered active carbon dosing
RO : reverse osmosis
SE : sedimentation
SF : sand filtration
SSF : slow sand filtration
UF : ultra filtration
UV : ultra violet