1 2	Glyphosate in the general population and in applicators: A critical review of studies on exposures
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²⁵ 1 Introduction

The recent classification of glyphosate as a probable human carcinogen by IARC 26 (2015), has generated considerable interest, particularly as the IARC classification was 27 arrived at without a detailed assessment of risk to applicators and the general public. 28 Glyphosate is widely used for control of weeds in agriculture, forestry, and in the man-29 agement of public and private landscapes. These uses might result in exposures of the 30 general public as well as applicators. Unfortunately, the IARC report merely focused on 31 the potential hazards of glyphosate and not on the risks. Exposure is a critical compo-32 nent of risk assessment and, without measured values, it is difficult to provide guidance 33 on the appropriate uses of glyphosate or, for that matter, any pesticide. It is also not 34 possible to properly assess toxicity and hazards data for relevance to humans and the 35 environment. 36

37

There are several sources of exposure of humans to glyphosate in environment. These are: Air, water, application to crops and target weeds, and food. The following sections are an analysis of exposures of humans to glyphosate from these sources. Data for these exposures were obtained from papers published in the open literature and from unpublished reports provided by Monsanto Company. These sources of information are listed in the references and summary data are provided in the supplemental information (SI).

45 **2 Methods**

Unpublished reports of studies on exposure to glyphosate in applicators were provided
 by Monsanto Company and covered uses in agriculture and forestry. Other data on exposures were obtained from the open literature as a result of searches in PubMed ®,
 references in reviews, and Google Scholar®. These papers and reports were grouped
 into sources of exposures and the data analyzed as described below.

51 **2.1 Air**

Only one paper reported concentrations of glyphosate in air. In a study conducted in 52 Iowa, Mississippi, and Indiana in 2007 and 2008, concentrations of glyphosate and its 53 major environmental degradate, aminomethylphosphonic acid (AMPA) were measured 54 in air and precipitation (Chang et al. 2011). Detections of AMPA were infrequent and 55 the concentrations small. These are not discussed further. The frequency of detection 56 of glyphosate ranged from 60 to 100% in air and rain-water. Concentrations in air 57 ranged from <0.01 to 9.1 ng/m³, while those in rain were from <0.1 to 2.5 µg/L. Con-58 centrations in air were seasonal and the sources were likely associated with application 59 to crops in the growing season. For estimation of human exposure, it was assumed that 60 there was total absorption of glyphosate from the air into the body of a 70 kg human 61 breathing 8 m³ air (half a day for an adult, USEPA 2009). These values were then used 62 to calculate the systemic dose, based on a worst-case assumption of 100% uptake via 63

65 **2.2 Water**

Glyphosate can enter surface waters through runoff and from drift of spray. Glyphosate 66 is very soluble in water and, although it binds strongly to soils and sediments, small 67 concentrations have been measured on surface waters in the USA. These measure-68 ments are part of the NAWQA program (USGS 2015), which has been in place for since 69 the 1980s. Glyphosate was added to the large range of analytes measured in surface 70 water in 2002. These data were downloaded from the NAWQA data warehouse and 71 then sorted by concentration. All values measured across the US between 2002 and 72 2014 were pooled for the analysis. Where concentrations were less than the level of 73 detection (0.02 µg glyphosate a.e./L), these values were substituted with a dummy val-74 ue of "zero". The values were ranked from smallest to largest and a cumulative fre-75 quency distribution derived. These values were processed using the Weibull formula to 76 estimate ranks and plotted on a log-probability scale (Solomon and Takacs 2002). The 77 median (50th centile) and 90th centile values were calculated from the raw data using the 78 Excel function <=percentile>. Systemic dose was estimated from the assumption of 79 consumption of 2 L of water per day by a 70 kg human. It was assumed that treatment 80 of the water did not remove any glyphosate. The estimated concentrations are thus a 81 worst-case. 82

83 2.3 Food and bystanders

Several studies have measured concentration of glyphosate in "bystanders" and people 84 not involved in application of glyphosate. These individuals are presumable exposed 85 via food, water, or air (see above). It is also assumed that these individuals are ex-86 posed on a daily basis through the environment and/or food and drinking water, and that 87 these exposures are constant and not episodic as in an applicator. Here a single daily 88 sample of urine is a reasonable surrogate for daily exposures. Several of these studies 89 were critically reviewed in 2015 (Niemann et al. 2015). This review was thorough but 90 the original studies were of variable strength of methods. In addition, the authors did 91 not correct for incomplete excretion of glyphosate (95%) as has been done for the ap-92 plicator studies. \In a study of farm and non-farm households in Iowa (Curwin et al. 93 2007), urine samples were analyzed from 95 adults and 117 children. A study in Eu-94 rope (Mesnage et al. 2012) measured exposures in a farm family (two adults and three 95 children). A report on the analysis of the urine of 182 people from 18 countries (Hoppe 96 2013) provided exposures in urine. In another study, urinary concentrations of 40 male 97 and female German students were measured (Markard 2014). The study was in Ger-98 man and the value listed for the systemic dose is from the review of Nieman et al. 99 (2015). A study using ELISA analysis with an unstated LOQ was conducted on more 100 than 300 individuals in the EU (most from Germany) (Krüger et al. 2014). A report of a 101 study in the US on 35 individuals using an ELISA analysis (Honeycutt and Rowlands 102 2014) provided data from which a systemic dose of was estimated. 103 104 Where the systemic dose was calculated, it was used. Where dietary exposures were 105

calculated the urinary concentration was used to calculate the systemic dose on the as-

- sumption of 2 L of urine per day and a 60 kg person (Niemann et al. 2015).
- 108

Under the auspices of the Food and Agricultural Organization of the United Nations, the
 Joint Meeting on Pesticide Residues (JMPR) conducts routine assessments of residues
 of pesticides in food (FAO 2013). These are evaluated in relation to diets in various re gions of the world and exposure via food compared to acceptable daily intakes (ADIs).
 In 2013, the JMPR reviewed dietary exposures to glyphosate (glyphosate, N-acetyl

glyphosate, AMPA and N-acetyl AMPA) and calculated the international estimated daily

intakes (IEDI) of glyphosate for 13 regional food diets (FAO 2013). These IEDIs were

based on estimated mean residues from supervised trails under normal or good agricul-

tural practice. The maximum IEDI was 762, the median was 301, and the minimum was

118 124 μ g/person/d. These values were normalized to a 60 kg person (12.7, 5.0, and 2.1

- $\mu g/kg b.m./d$, resp.) for comparison to the ADI.
- 120

The USEPA has calculated exposures to glyphosate using the Dietary Exposure Evaluation Model (DEEM), which based on tolerance levels for all commodities and modeled estimates of exposures from drinking water (USEPA 2014). The dietary exposure esti-

mated by USEPA is 0.087 mg/kg b.m./d (USEPA 2013).

125 2.4 Applicators

A relatively large number of studies on exposures of applicators to glyphosate have

been conducted (see SI for a full list). Older studies tended to use passive dosimetry,
 either as whole-body dosimeters or patches. Some of the studies with dosimeters used

tracers (dyes or other surrogates) and others analyzed dosimeters for glyphosate itself.

Some more recent studies used biological monitoring and some a mixture of biological

monitoring and patches. For compounds, such as glyphosate, where the excretion ki netics is well understood, biological monitoring provides a measure of the actual amount
 of the chemical in body. For this reason, data from these studies are the most appro priate for risk assessment. However, data from dosimetry studies can be used to esti-

mate systemic dose. This allows comparison of exposures from different studies to a
 benchmark for exposure i.e., the RfD or ADI.

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For studies using dosimetry, the normalization to systemic dose was conducted using the procedure outlined in Table 1. This was done for the dosimetry studies listed in SI Table 1. The estimated systemic doses were ranked from smallest to largest and a cumulative frequency distribution derived. These values were plotted on a log-probability scale as above. The median (50th centile) and 90th centile values were calculated from the raw data using the Excel function <=percentile>.

144 145

Table 1. Procedure for normalization of dosimetry data to estimate systemic dose.

Step	From		То	Explanation
1	Total residue on patches µg/cm²)	to	Potential body ex- posure (µg)	2.1 m ² surface area for a 70 kg male (USEPA 2009)
2	Potential body expo- sure (µg)	to	Actual body expo- sure (μg)	Measured penetration through clothing or default of 10%
3	Actual body exposure (µg)	to	Systemic body ex- posure (µg)	1% dermal penetration (from the value used by EFSA 2015).
4	Systemic body expo- sure (µg)	to	Systemic dose (mg/kg b.w./day)	70 kg adult.

Where an applicator makes a single application, the systemic dose of glyphosate can be estimated from the total amount of glyphosate excreted in the urine over the four or five days following and including the day of application (Acquavella et al. 2004). If ap-

- plications are conducted every day, the amount excreted each day provides a time-
- 151 weighted average for daily exposures. Because glyphosate is applied infrequently in
- normal agricultural practice, the assumption of a single initial exposure is appropriate for
- risk assessment.
- 154

The procedure of normalization for biomonitoring studies is complicated by the fact that 155 many studies reported concentrations of glyphosate that are less than the level of quan-156 titation (LOQ), even on the day of application (d-0), when exposures would be expected 157 to greatest. Similarly, even if residues were detected on d-0, those on subsequent days 158 might have values less than the LOQ. The common practice of using half the level of 159 detection as a default value might be acceptable for the first observation day, but this 160 fails to account for excretion which would reduce the amount in the body on each suc-161 cessive day. Use of half the LOQ on each day would grossly overestimate the systemic 162 dose. Because of this, normalization of systemic doses was modeled using excretion 163

kinetics and followed the steps outlined in Table 2.

165

166 Table 2. Procedure for normalization of dosimetry data to estimate systemic dose.

Step	Data	Action
1	LOD = 10 µg/kg urine	Assume half the LOD = 5 μg/kg
2	Adjust estimated dose to amount of urine	Multiple kg urine produced on day by 1/2 LOD
3	D-0 value amount estimated	C₀ amount
4	D-1 value estimated from remainder of d-0 concentration after excretion	Elimination rate constant (k) of 0.86 d ⁻¹ from (Acquavella et al. 2004) use C_t . = $C_0 \times e^{-kt}$
5	D-2 value estimated from remainder of d-1 concentration after excretion	
6	D-3 value estimated from remainder of d-2 concentration after excretion	
7	D-4 value estimated from remainder of d-3 concentration after excretion	
8	D-5 value estimated from remainder of d-4 concentration after excretion	
9	Sum of amounts for each day of urine col- lected	
10	Correction for monitoring period from elimina- tion rate constant and number of days	For example 99% for 5 d, divide by 0.99
11	Correction for incomplete excretion (95%)	Based on observations in TK studies in mon- keys which showed that 95% of total systemic dose was excreted via urine, divide by 0.95.
12	Correction for dosimeters, if used	Increase dose by percentage of body area rep- resented by the dosimeters
13	Correction for hand wash or gloves, if used	Increase dose by percentage of body area rep- resented by hands
14	Calculate systemic dose	Divide total systemic dose by body mass.

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If concentrations in urine are >LOQ for one or more days, the actual elimination rate for
 the individual can be used to correct for days where concentration is <LOQ. Unless al-

ready carried out in the study itself, these corrections were applied to the data in SI Ta-ble 2.

2.5 Normalization of the RfD and ADI for systemic dose

Regulatory agencies set allowable limits for glyphosate exposure based on toxicity studies. The USEPA RfD is 1.75 mg/kg b.m./day (USEPA 2012). The ADI for JMPR/WHO is 1 mg/kg b.m./d (FAO 2013), while the ADI used by EFSA is 0.5 mg/kg b.m./d (EFSA 2015). These values are suitable for comparison to the dietary intake but for comparison to systemic doses as estimated from biological monitoring (urinary excretion) the ADIs and RfD are divided by 5 to account for only 20% absorption from the GI tract (EFSA 2015). These normalized values are 0.35, 0.2, and 0.1 mg/kg b.m./d, resp.

180 **3 Results**

181 **3.1 Air**

Based on the above assumptions, inhaling glyphosate in air at the maximum measured concentration would result in an exposure of 1.04×10^{-6} mg/kg b.m./d. This is about 6orders of magnitude less than the current USEPA's RfD of 1.75 mg/kg b.m./d.

185 3.2 Water

186 The cumulative

- 187 frequency distri-188 bution of con-
- centrations of
- 190 glyphosate
- 191 measured in sur-
- 192 face waters of
- 193 the US are
- 194 shown in Figure
- 195 1. The 50th cen-
- tile concentration
- 197 was 0.06 µg/L
- and the 90th cen-
- tile was 0.79
- μg/L. The maxi-
- 201 mum concentra-
- tion measured
- 203 was 73 μg/L.
- 204 Consumption of
- 205 2 L of drinking
- water by a 70 kg
- 207 person at the
- 208 90th centile con-
- centration is es-
- timated to result in a systemic dose of 2.25 x 10^{-5} mg/kg b.m./d. Normalized for absorp-
- tion from the gut, this value is about 1.6×10^{-4} less than USEAP's RfD.

face waters across the US.



3.3 Food and bystanders

Estimates of the systemic dose resulting from exposures of bystanders and the general public to glyphosate are shown in Table 3.

215

Study	Source of Ex-	Urinary C tration	Urinary Concen- tration (ug/L)		ic dose b.m./d)	Comment
		Greatest	Maxi-	Greatest	Maxi-	-
		Mean	mum	Mean	mum	
(Table 2 from	Presumably	2.7	9.4	0.00009	0.00031	Highest mean
Curwin et al.	food and water					and max was in
2007)	from non-farm					non-farm children
	households in					
(Table 2 frame	IOWA	0.4		0 00007		Llight and usedian
	form households	2.1		0.00007		Highest median
2007)	in Iowa					dren Max not
2007)	III IOWA					reported
(Mesnage et al.	Bvstander, farm		2		0.00007	Maximum con-
2012)	family of five					centration in child
(Hoppe 2013)	Presumably	0.82	1.82	0.000027	0.000061	Highest mean
	food and water					was in samples
						from Malta
(Markard 2014)	Presumably		0.65		0.000022	Maximum con-
	food and water		_			centration
(Krüger et al.	Presumably		5		0.00017	Maximum con-
2014)	food and water		10.0			centration
(Honeycutt and	Presumably		18.8		0.00063	Maximum con-
Rowlands 2014)	tood and water					centration

Table 3. Summary of glyphosate exposures of bystanders and the general public.

Systemic dose (mg/kg b.m./d) = Urinary concentration (μ g/L) x 2 L urine/day \div 60 kg body mass x 1000

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All of these systemic doses (Table 3) are three or more orders of magnitude less than the USEPA's RfD normalized for reduced uptake from the gut.

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Based on the estimates of daily intake from the FAO/JMPR, median exposures are 340

times less than the USEPA's RfD and 200 times less than the ADI suggested but FAO/JMPR.

224 3.4 Applicators

For the applicator studies, the corrections were applied as in Table 1 or Table 2 and the results are presented graphically in Figure 2. Raw data are provided in SI Tables 1, and 2.

228

The range of values for systemic doses measured in the dosimeter studies was greater than in the biomonitoring studies. Given the corrections applied to the data, this is sur-

prising; however, there are a number of assumptions used in the normalization of the

systemic doses that might result in overestimation of exposure. These are likely in the

amount of absorption though skin and the penetration of clothing. The assumption of

1% penetration through the skin is greater than the value of 0.7% suggested from ob-

servations in an in vitro model with human skin (Bo Nielsen et al. 2009). The 50th and

²³⁶ 90th centiles in the dosimetry studies were 0.0005 and 0.021 mg/kg b.m./d, respectively.

- Neither of these values is particularly large when compared to the USEPA's normalized
 RfD of 0.035 mg/kg b.m./d.
- 239

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268

The range of val-240 ues for the sys-241 temic doses de-242 termined by bio-243 monitoring was 244 smaller than for 245 the passive do-246 simeters and more 247 accurately reflects 248 the true expo-249 sures. The 50th 250 and 90th centiles 251 were 0.0003 and 252 0.0014 mg/kg 253 b.m./d, respective-254 ly. These are sev-255 eral orders of 256 magnitude less 257 than the USEPA's 258 normalized RfD. 259 260



Figure 2. Systemic doses of glyphosate measured in exposure studies conducted in applicators.

262 4 Conclusions

Even when using a number of worst-case assumptions, systemic doses of glyphosate in human applicators, bystanders, and the general public are very small. Those in the general public are three or more orders of magnitude less than the USEPA's RfD and in the most exposed applicators (90th centile) the systemic dose was estimated at 10-fold less that the normalized RfD.

Overall, there is a robust data-set on exposures of applicators and the general public to glyphosate. All of these exposures are less than the RfD or the ADIs, some by many orders of magnitude. As an overall summary, these are shown graphically in Figure 3. Based on current RfDs and ADIs, there is no hazard from exposure to glyphosate via its normal use in agriculture and management of landscapes.



Figure 3. Illustration of measured and estimated exposures to glyphosate in applicators and the general public from various sources. Red stars indicate the RfD and the ADIs and the blue stars the same values normalized to systemic dose. Solid horizontal bars show 10th - 90th centiles, whiskers show minimum and maximum.

275 276

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- 384

385 6 Supplemental information

386 SI Table 1. Normalized systemic exposures to glyphosate conducted with passive dosimetry

Study	Event	Technique	ID	Test Item	Sys-dose mg/kg/d
(Kramer 1978)	Re-entry DAY7	Other	Patch	Glyphosate	5.43E-07
(Kramer 1978)	Handgun - tractor	Tractor	Patch	Glyphosate	1.22E-06
(Kramer 1978)	Boom spray	Tractor	Patch	Glyphosate	1.31E-06
(Kramer 1978)	Handgun - tractor	Tractor	Patch	Glyphosate	1.95E-06
(Cowell and Steinmetz 1990a)	Scout	Other	Patch	Glyphosate	2.30E-06
(Kramer 1978)	Boom spray	Tractor	Patch	Glyphosate	3.16E-06
(Kramer 1978)	Re-entry DAY1-2	Other	Patch	Glyphosate	3.39E-06
(Kramer 1978)	Backpack	Handheld	Patch	Glyphosate	4.22E-06
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	4.47E-06
(Machado-Neto et al. 2000)	Mixer	Mixer	Patch	Tracer	9.49E-06
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	9.57E-06
(Kramer 1978)	Tank fill	Mixer	Patch	Glyphosate	9.71E-06
(Kramer 1978)	Handgun - tractor	Tractor	Patch	Glyphosate	9.74E-06
(Kramer 1978)	Backpack	Handheld	Patch	Glyphosate	1.23E-05
(Kramer 1978)	Handgun	Handheld	Patch	Glyphosate	1.51E-05
(Kramer 1978)	Re-entry DAY1-1	Other	Patch	Glyphosate	1.55E-05
(Kramer 1978)	Re-entry DAY3	Other	Patch	Glyphosate	1.72E-05
(Kramer 1978)	Backpack	Handheld	Patch	Glyphosate	2.66E-05
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	2.82E-05
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	3.09E-05
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	3.14E-05
(Kramer 1978)	Boom spray	Tractor	Patch	Glyphosate	3.15E-05
(Machado-Neto et al. 2000)	Backpack	Handheld	Patch	Tracer	3.99E-05
(Cowell and Steinmetz 1990a)	Appl.	Tractor	Patch	Glyphosate	4.52E-05
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	4.99E-05
(Machado-Neto et al. 2000)	Backpack	Handheld	Patch	Tracer	5.40E-05
(Cowell and Steinmetz 1990b)	Mixer	Mixer	Patch	Glyphosate	6.30E-05
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	6.66E-05
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	7.10E-05
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	7.25E-05
(Kramer 1978)	Handgun	Handheld	Patch	Glyphosate	7.37E-05
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	7.44E-05
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	7.64E-05
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.01E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	1.05E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	1.07E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	1.31E-04
(Cowell and Steinmetz 1990b)	Mixer	Mixer	Patch	Glyphosate	1.63E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	1.76E-04
(Machado-Neto et al. 2000)	Mixer	Mixer	Patch	Tracer	1.85E-04
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.85E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	2.03E-04
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	2.06E-04
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	2.11E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	2.37E-04

(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	2.48E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	2.71E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	2.78E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	2.94E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	3.07E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	3.07E-04
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	3.09E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	3.09E-04
(Machado-Neto et al. 2000)	Spray application	Tractor	Patch	Tracer	3.42E-04
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	3.88E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	4.03E-04
(Kramer 1978)	Handgun	Handheld	Patch	Glyphosate	4.13E-04
(Kramer 1978)	Mixer	Mixer	Patch	Glyphosate	4.25E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	4.63E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	4.66E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	4.84E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	4.99E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	5.05E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	5.66E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	6.37E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Patch	Glyphosate	6.81E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	7.28E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	7.56E-04
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	8.50E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	8.94E-04
(Edmiston et al. 1995)	Mix/load/application	Right of way	Whole	Glyphosate	9.38E-04
(Tan et al. 1987)	Mixer	Mixer	Day 3	Tracer	1.01E-03
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.12E-03
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.13E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	1.25E-03
(Cowell and Steinmetz 1990a)	Appl.	Tractor	Patch	Glyphosate	1.29E-03
(Cowell and Steinmetz 1990a)	Weeder	Other	Patch	Glyphosate	1.34E-03
(Kramer 1978)	Mixer	Mixer	Plot 4,5,6	Glyphosate	1.45E-03
(Tan et al. 1987)	Mixer	Mixer	Patch	Tracer	1.46E-03
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.61E-03
(Cowell and Steinmetz 1990a)	Weeder	Other	Patch	Glyphosate	1.74E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	2.16E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	3.11E-03
(Kramer 1978)	Mixer	Mixer	Patch	Glyphosate	3.42E-03
(Tan et al. 1987)	Mixer	Mixer	Patch	Tracer	3.65E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	3.71E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	4.28E-03
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	4.53E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	5.16E-03
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	6.28E-03
(Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	6.29E-03
(Momesso and Machado Neto	Application	Tractor	Whole	Tracer	7.58E-03
2003) (Momesso and Machado Neto	Application	Tractor	Whole	Tracer	7.74E-03
2003) (Manning 1991)	Mistblower	Handheld	Patch	Glyphosate	8.01E-03
				, · · · · · · · · · · · · · · · · · · ·	

(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	8.19E-03
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	8.32E-03
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	8.66E-03
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	9.15E-03
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	1.02E-02
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	1.11E-02
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	1.14E-02
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	1.18E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	1.29E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	1.30E-02
(Johnson et al. 2005)	CDA	Handheld	Patch	Glyphosate	1.65E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	1.81E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	1.82E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	2.11E-02
(Tan et al. 1987)	Backpack	Handheld	Patch	Tracer	2.13E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	2.30E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	2.56E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	2.64E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	2.94E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	3.01E-02
(Tan et al. 1987)	Mixer	Mixer	Patch	Tracer	3.61E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	3.73E-02
(Cowell and Steinmetz 1990a)	Appl	Tractor	Patch	Glyphosate	4.64E-02
(Tan et al. 1987)	Mixer	Mixer	Patch	Tracer	4.93E-02
(Momesso and Machado Neto 2003)	Application	Tractor	Whole	Tracer	5.61E-02
(Tan et al. 1987)	CDA	Handheld	Patch	Tracer	6.39E-02
(Tan et al. 1987)	Mixer	Mixer	Patch	Tracer	6.40E-02
CDA = Controlled Droplet	Applicator			50 th centile	0.0005
				90 th centile	0.021

SI Table 2. Normalized systemic exposures to glyphosate conducted with biomonitoring

Study	Activity	Application technique	Dosimeter	Test item	Sys-dose mg/kg/d
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	1.30E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	2.13E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.41E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.54E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.64E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	2.69E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	2.74E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.76E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.80E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.92E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.09E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.24E-05

		Application			Sys-dose
Study	Activity	technique	Dosimeter	Test item	mg/kg/d
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.26E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	3.40E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.58E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	3.63E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.74E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.81E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.11E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.28E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.45E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.63E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.66E-05
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	5.21E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	5.36E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	5.80E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	5.88E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	6.38E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	6.54E-05
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	6.59E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	6.60E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	6.75E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	7.00E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	7.09E-05
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	7.26E-05
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	7.62E-05
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	8.28E-05
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	9.48E-05
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	1.01E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.03E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.05E-04
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	1.11E-04
(Placka 2007)	Paaknaak	Puro unshield-	Urino	Clumbosoto	
(Abdolghopi 1005)	Spray application	eu Diabt of wow	Unne	Glyphosate	1.13E-04
	Spray application	Right of way	Unne	Giyphosate	1.10E-04
(Acquavella et al. 2004)	Spray application	Applicator	Unne	Giyphosate	1.19E-04
(Dieeke 2007)	Баскраск	Applicator	Unne	Glyphosate	1.20E-04
(Cowell and Stellinetz 1990a)	Аррі.	Puro unshield-	Unne	Giyphosate	1.29E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	1.39E-04
(Cowell and Steinmetz 1990a)	Appl.	Tractor	Urine	Glyphosate	1.40E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	1.44E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	1.61E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	1.67E-04
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	1.71E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.74E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	1.80E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.84E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.92E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.06E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	2.12E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.20E-04

Study	Activity	Application technique	Dosimeter	Test item	Sys-dose ma/ka/d
(Cowell and Steinmetz 1990b)	Backpack	Handbeld	Urine	Glyphosate	2 50E-04
(Cowen and Steinmetz 1990b)	Spray application	Tractor	Patch	Glyphosate	2.50E-04
	opray application	Puro unshield-	1 atom	Olyphosate	2.022-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	2.53E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	2.58E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	2.64E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	2.74E-04
(Bleeke 2007)	Backpack	Mixer Puro unshield-	Urine	Glyphosate	2.76E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	2.80E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	2.84E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.91E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	2.96E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	3.12E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	3.20E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	3.29E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	3.44E-04
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	3.52E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	3.55E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	3.68E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	3.71E-04
(Cowell and Steinmetz 1990b)	Mixer	Mixer	Urine	Glyphosate	3.74E-04
(Bleeke 2007)	Backpack	Applicator	Urine	Glyphosate	3.85E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	3.91E-04
(Abdelghani 1995)	Spray application	Right of way Puro unshield-	Urine	Glyphosate	3.91E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	3.95E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	4.01E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.01E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	4.15E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	4.15E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	4.19E-04
(Bleeke 2007)	Backpack	Applicator Puro unshield-	Urine	Glyphosate	4.20E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	4.39E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	4.69E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.74E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.80E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	4.81E-04
(Cowell and Steinmetz 1990a)	Appl.	Tractor	Urine	Glyphosate	5.09E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	5.34E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	5.43E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	5.50E-04
(Bleeke 2007)	Backpack	Puro shielded	Urine	Glyphosate	5.51E-04
(Acquavella et al. 2004)	Spray application	Tractor Puro unshield-	Urine	Glyphosate	5.71E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	5.89E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	6.16E-04
(Cowell and Steinmetz 1990b)	Mixer	Mixer Puro unshield-	Urine	Glyphosate	6.82E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	6.98E-04
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	7.04E-04

Study	Activity	Application technique	Dosimeter	Test item	Sys-dose mg/kg/d
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	7.35E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	8.33E-04
(Bleeke 2007)	Backpack	Applicator Puro unshield-	Urine	Glyphosate	8.48E-04
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	8.80E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	8.83E-04
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	8.89E-04
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.15E-03
(Cowell and Steinmetz 1990a)	Appl.	Tractor Puro unshield-	Urine	Glyphosate	1.27E-03
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	1.37E-03
(Bleeke 2007)	Backpack	Puro shielded Puro unshield-	Urine	Glyphosate	1.37E-03
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	1.50E-03
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	1.51E-03
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	1.53E-03
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	1.59E-03
(Abdelghani 1995)	Spray application	Right of way Puro unshield-	Urine	Glyphosate	1.68E-03
(Bleeke 2007)	Backpack	ed	Urine	Glyphosate	1.72E-03
(Bleeke 2007)	Backpack	Mixer	Urine	Glyphosate	2.07E-03
(Acquavella et al. 2004)	Spray application	Tractor	Urine	Glyphosate	2.28E-03
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	2.39E-03
(Jauhiainen et al. 1991)	Brush-saw	Handheld	Urine	Glyphosate	2.61E-03
(Cowell and Steinmetz 1990b)	Backpack	Handheld	Urine	Glyphosate	2.74E-03
(Abdelghani 1995)	Spray application	Right of way	Urine	Glyphosate	4.56E-03
				50 th centile	0.0003
				90 th centile	0.0014

Removal and degradation of glyphosate in water treatment: a review

Jörgen Jönsson, Rob Camm and Tom Hall

ABSTRACT

Glyphosate is a broad spectrum, non-selective herbicide, widely used for the post-emergence control of annual and perennial weeds in a variety of applications. Although of low toxicity, its presence in drinking water is undesirable and can cause drinking water compliance failure in the EU if found at concentrations $>0.1 \,\mu$ g L⁻¹. Treatment methods such as ozonation and activated carbon are currently used for pesticide degradation and removal. This article provides a review of the reported efficiency in removal and degradation of glyphosate and aminomethylphosphonic acid (AMPA) by some commonly employed treatment options. Additional experiments have been carried out where knowledge gaps have been identified. Oxidants used in water treatment, particularly Cl₂ and O₃, are highly effective in degrading glyphosate and AMPA. Removal by coagulation and activated carbon is ineffective as a barrier against contamination in drinking water. UV treatment is also ineffective for glyphosate, but not AMPA, under the combination of UV/H₂O₂ provided significant degradation by bank filtration, slow sand filtration, ClO₂ and membranes is variable but can provide significant removal under the right conditions.

Key words AMPA, drinking water, glyphosate, removal, review, treatment

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INTRODUCTION

Glyphosate (N-(phosphonomethyl)-glycin, H_2O_3P -CH₂-NH-CH₂-COOH) is a broad spectrum, non-selective herbicide, widely used for the post-emergence control of annual and perennial weeds. Glyphosate acts by inhibiting the shikimic acid pathway, a biochemical pathway present in plants, but not in animals (DellaCioppa *et al.* 1986). Glyphosate has a low potential to reach groundwater due to strong soil binding properties (Sprankel *et al.* 1975; Glass 1987; Sheals *et al.* 2002) and biodegradability in soil (Sprankel *et al.* 1975; Olawale & Akintobi 2011), but may reach surface water from other routes, such as spray drift, runoff and drainage, as well as point source contamination.

The European Council Directive 98/83 (1998) related to the quality of water for human consumption sets a limit of $0.1 \ \mu g \ L^{-1}$ for individual pesticides, their relevant metabolites, decay and reaction products and $0.5 \ \mu g \ L^{-1}$ for doi: 10.2166/aqua.2013.080 total pesticide concentration. This blanket standard applies to glyphosate, despite its low toxicity (Hayes & Laws 1991; Klaassen 2001). The US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of $700 \,\mu g \, L^{-1}$ for glyphosate in drinking water and WHO have considered it unnecessary to derive a guideline value for glyphosate in drinking water (WHO 2005).

Aminomethylphosphonic acid (AMPA, $H_2O_3P-CH_2-NH_2$) is the only significant metabolite of glyphosate. It is readily produced from glyphosate by microorganisms and is therefore included in reviews of glyphosate removal in water treatment. AMPA is chemically similar to glyphosate and shows similar properties in terms of behaviour and toxicity. However, there are additional 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; Jadas-Hécart *et al.* 2010).

The use of glyphosate has steadily increased (Coupe *et al.* 2012), it is undesirable in water supply and would cause compliance failure for water companies in the EU if found above $0.1 \,\mu g \, L^{-1}$ in drinking water. This paper provides a review of different treatment options to remove or degrade glyphosate and AMPA in water treatment, including what are commonly known as advanced oxidation processes (AOPs). AOPs include some combination of O₃, UV, H₂O₂ and TiO₂. Some knowledge gaps were identified in the literature and laboratory tests were undertaken to provide further information. Parts of the review in this work have previously been reported (Hall & Camm 2007).

METHODS

Batch tests were carried out to investigate the degradation of glyphosate and AMPA by oxidation using Cl₂, ClO₂, O₃, O₃/H₂O₂, and by adsorption using PAC (powdered activated carbon). The stock solutions of glyphosate and AMPA were prepared by dissolving high purity solids in deionised water. Tap water, purged with air to remove residual chlorine, was spiked with stock solutions to achieve a concentration of $3 \mu g L^{-1}$ of either glyphosate or AMPA. This concentration was chosen to represent a moderately contaminated water (WHO 2005; Reily et al. 2011; Coupe et al. 2012). Samples of the spiked water were taken for analysis to establish the initial concentration of glyphosate and AMPA. In the oxidation tests with glyphosate spiking, the treated water samples were also analysed for AMPA. to investigate whether any of the glyphosate was degraded only to AMPA.

For the ozonation tests, preliminary tests were carried out to find suitable settings to achieve a residual of approximately 0.2–0.4 mg $O_3 L^{-1}$ after a contact time of 15 min. It was not possible to calculate the ozone dosed or transferred during the tests, but residual levels and contact times in the tests were representative of those occurring in full scale plant. A 1 L sub-sample of spiked water was ozonated using a pilot-scale O_3 generator (Labo II ozonator from Ozotech Ltd) and a bubble diffuser stone. Following ozonation, the O_3 residual was measured immediately, and at 5 min intervals, during a 15 min contact time. At the end of the contact period, the residual ozone concentration was quenched with sodium thiosulphate. A further set of tests was carried out with simultaneous use of O_3 and H_2O_2 , at 0.5 and 1.0 mg L⁻¹ of H_2O_2 . The ozonation conditions were identical to the test with O_3 alone. At the end of the contact period, the residual O_3 and H_2O_2 were quenched with sodium thiosulphate as above.

For the chlorine tests, 1 L samples of the spiked water were dosed with sodium hypochlorite at 1.5 mg $Cl_2 L^{-1}$. The dosed water was left for 30 min at the desired temperature. At the end of the contact period, the residual Cl_2 was measured and then quenched with sodium thiosulphate as above. The tests with Cl_2 were repeated but with ClO_2 as the oxidant. The ClO_2 was added as crushed tablets (Accepta). The initial target concentration of ClO_2 was 1 mg L^{-1} .

Tests were carried out to investigate the performance of three different types of coal based PAC; Norit W35, Norit SA Super and Chemviron W. One litre samples of the spiked water were dosed with the three different PAC products at 5, 15, and 25 mg L^{-1} . The dosed water was left stirring at room temperature for 1 h to keep the PAC in suspension. The samples were then filtered through GF/C grade filter paper to remove the carbon prior to analysis for glyphosate and AMPA.

The initial results for AMPA showed large variations, even for the spiked untreated control samples. This was found to be caused by a rapid degradation of AMPA by the low concentrations of free chlorine present in the tap water used ($<0.2 \text{ mgCl}_2 \text{ L}^{-1}$). Tap water for the subsequent oxidation tests was thoroughly purged with air for 72 h to remove the free chlorine before addition of AMPA. This changed the pH from 7.5 to 8.4. The free chlorine concentration in the purged water was $<0.02 \text{ mg L}^{-1}$. This rapid degradation of AMPA by chlorine in the control samples was not apparent for glyphosate.

The effects of UV, UV/H₂O₂, O₃, O₃/H₂O₂, and UV/ O₃/H₂O₂ were investigated in a flow through pilot reactor from ITT Wedeco, consisting of in-line H₂O₂ dosing, O₃ dosing and a UV reactor, which could be used individually or in combination. The retention time in the unit was 0.5– 1 min, most of which occurred in the UV reactor which has a single low pressure, high output germicidal UV lamp (254 nm, input power to the lamp 330 W). The UV dose is governed by changing the flowrate through the unit, and doses of H_2O_2 and O_3 can then be set independently. Two tests were performed, each with the same matrix of operating conditions. The feed tank was filled with 2 m³ of tap water and then left for a minimum of 7 days, during which the free and total chlorine residuals were monitored. Free chlorine residual declined to below the limit of detection (LOD) within 48 h. The feed tank was then spiked with glyphosate or AMPA at a target concentration of 3 µg L⁻¹ and the water recirculated to ensure the compound was evenly distributed.

The concentrations of O_3 , H_2O_2 , Cl_2 and ClO_2 were analysed by test kits (Palintest). Glyphosate and AMPA were analysed by Severn Trent Services using the method reported by Lee *et al.* (2002). Samples were treated with 9fluorenylmethyl chloroformate derivatising reagent prior to concentration by solid phase extraction. The extracts were analysed by high-performance liquid chromatography/ mass spectrometry detection in negative ion electrospray with selective ion monitoring. The reported recovery up to $0.3 \mu g/L$ was 99% with a LOD of $0.006 \mu g/L$. The results presented are for single samples.

REVIEW OF WATER TREATMENT REMOVAL AND DEGRADATION

Bank filtration

Whilst not strictly a treatment process, abstraction of surface water through a natural terrestrial matrix and mixing with groundwater, such as occurs with bank filtration and similar processes, has been found to remove a proportion of both glyphosate and AMPA. Lange & Post (2000) found a progressive reduction in AMPA with increasing distance between abstraction and the River Main at Eddersheim in Germany, from $0.34 \ \mu g \ L^{-1}$ in the river to $0.06 \ \mu g \ L^{-1}$ at a distance of 190 m from the river. The concentration of glyphosate in the source and abstracted water was less than the LOD ($0.05 \ \mu g \ L^{-1}$). Ijpelaar *et al.* (2000) reported concentrations of up to $0.49 \ \mu g \ L^{-1}$ glyphosate and $5.4 \ \mu g \ L^{-1}$ 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. Other studies (Hopman *et al.* 1995; Schlett *et al.* 2005) also indicate removal of up to 95% of AMPA by bank filtration, but concurrent concentration measurements for glyphosate were too small to draw conclusions. Getenga & Kengara (2004) reported 95% removal of glyphosate after 50 days in aerobic batch soils samples at an initial concentration of $100 \ \mu g \ g^{-1}$.

It is well known that glyphosate and AMPA readily adsorb to soil and degrade, so removal by bank filtration would be expected. The extent to which this occurs will depend on the time of passage of the water, the properties of the soil and the microbial community. The general trend in the literature reviewed is that the concentration of AMPA is higher than glyphosate but that AMPA is more readily degraded or removed. The degradation of glyphosate seems to benefit from aerobic conditions whereas AMPA is readily degraded both under aerobic and anaerobic conditions. Post et al. (2000) reported a removal between 17 and >30% for glyphosate and 46-87% for AMPA in anaerobic bank filtration and Stuyfzand et al. (2004) reported 85-94% removal of AMPA in anaerobic bank filtration. Lindner et al. (2000) reported >95% glyphosate removal in aerobic soil column tests. Alternating redox conditions (aerobic and anaerobic) are generally likely to improve the removal of organic contaminants as some compounds are more readily degraded under aerobic conditions and some are more susceptible to degradation under anaerobic conditions.

Chemical coagulation and clarification/filtration

Speth (1993) reported poor removal of glyphosate by coagulation with aluminium sulphate, followed by filtration. However, it should be noted that the turbidity of the filtered water was relatively high (2 NTU), suggesting non-optimal conditions which may well have biased the results. Hopman *et al.* (1995) evaluated different coagulants at four locations. The concentration of AMPA in the raw water (0.26–0.88 μ g L⁻¹) was reduced at three out of four of the sites by 49 to 83%. At the fourth site there was little or no removal, possibly due to the type of floc separation process (upflow filtration). Removal of glyphosate was less easily assessed at this site, due to very low initial concentrations. Kempeneers (2000) studied the removal of glyphosate and AMPA, using an aluminium based coagulant to treat a spiked river water. For coagulation and flotation, the average removal efficiency was 16 and 19% for glyphosate and AMPA, respectively. For coagulation and dual layer filtration, the removal increased to 40 and 26% for glyphosate and AMPA, respectively. The initial concentrations were 1 and $5 \mu g L^{-1}$ for glyphosate and AMPA, respectively. Lange & Post (2000) reported that the raw water concentration (0.1 μ g L⁻¹ glyphosate and 0.32 μ g L⁻¹ AMPA) was reduced by coagulation and flocculation by $39 \pm 14\%$ for glyphosate and $22 \pm 15\%$ for AMPA. At a full scale treatment works Ijpelaar et al. (2000) reported approximately 90% reduction of AMPA by coagulation/clarification, for an influent concentration of $1.8-3.3 \ \mu g \ L^{-1}$. 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 >7for 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. Roche et al. (2004) studied the removal of glyphosate and AMPA by coagulation, using a surface water spiked with glyphosate $(1 \ \mu g \ L^{-1})$. Either aluminium polychlorosulphate (WAC, 30 mg L^{-1}) or ferric chloride (30–70 mg L⁻¹) were used as coagulants. Ferric chloride showed best removal of both glyphosate and AMPA, up to 88 and 70%, respectively. The removal by ferric chloride was also less affected by pH compared to WAC. WAC showed an optimum removal at pH 6 (69 and 40% removal of glyphosate and AMPA, respectively) and the efficiency reduced markedly at both more acidic and alkaline conditions.

The performance of coagulation for incorporation of particulates from the water and the formation of stable floc particles is strongly dependent 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 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. Removal is reported to be more efficient when floc separation is achieved by filtration rather than flotation, which would be consistent with adsorption of the compounds on to particulates, and subsequently more efficient particulate removal occurring by filtration compared with flotation. As flotation is usually a pre-treatment before filtration, this finding is not of practical relevance to water treatment.

Slow sand filtration

Limited data for slow sand filtration (SSF) indicate a range of performance for removal of glyphosate and AMPA. 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 by SSF at two locations. For five measurements, glyphosate was below the LOD; AMPA was reduced from concentrations up to a maximum of $0.48 \ \mu g \ L^{-1}$, to $<0.05 \ \mu g \ L^{-1}$ (>80% removal). Schlett *et al.* (2005) studied the effect of SSF where the inlet water contained $<0.05-0.19 \ \mu g \ L^{-1}$ glyphosate, reducing to $<0.08 \ \mu g \ L^{-1}$ after filtration. The concentration of AMPA was in the range $<0.08-0.7 \ \mu g \ L^{-1}$ at the inlet, and was reduced to $<0.08 \ \mu g \ L^{-1}$ after filtration.

Chlorination

The literature suggests that chlorine is highly effective in reducing the concentration of glyphosate and AMPA at the concentrations and contact time typical for water treatment. The performance of chlorine will be temperature and pH dependent, but little information related to the impact of these factors was found. Hopman *et al.* (1995) found that when chlorine was dosed for distribution chlorination (0.2–0.6 mg L⁻¹ chlorine), between 40 and 100% of AMPA was degraded for initial concentrations of 0.2–5 µg L⁻¹. A chlorine dose of 2 mg L⁻¹ degraded >98% AMPA. Contact times were not stated. 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. Speth (1993) carried out tests with river water spiked with 739 μ g L⁻¹ of glyphosate. With an applied chlorine dose of 2.1 mg L^{-1} , the glyphosate concentration was reduced below the LOD ($25 \mu g L^{-1}$) after 7.5 min contact. Temperature and pH conditions were not described. Kempeneers (2000) carried out extensive tests on the degradation of AMPA and glyphosate with chlorine. In the first series of tests, 1.2 μ g L⁻¹ glyphosate was found to be completely degraded by a chlorine dose of 2 mg L^{-1} , after a contact time of 20 min, and 0.56 μ g L⁻¹ AMPA was degraded for the same conditions. A concentration of $5 \mu g L^{-1}$ glyphosate was degraded by a chlorine dose of 0.75 mg L^{-1} , after a contact time of 4 hours, and $0.42 \,\mu g \, L^{-1}$ AMPA was degraded under the same conditions. After a contact time of 120 seconds, $11.5 \ \mu g \ L^{-1}$ glyphosate and $0.14 \ \mu g \ L^{-1}$ AMPA were completely degraded, indicating fast kinetics. Lange & Post (2000) found that a chlorine concentration of 0.08 mg L^{-1} Cl₂ achieved 74 and 80% degradation of glyphosate and AMPA respectively, for a drinking water spiked at 0.05–0.4 μ g L⁻¹, after a contact time of 5 min. A chlorine dose of 0.40 mg L^{-1} achieved 94% degradation.

Generally, degradation is >95% except for the Lange & Post (2000) tests where the degradation (74%) was probably limited by a low chlorine dose and short contact time, and/or limitations in the analysis and calculation due to

glyphosate concentrations close to the LOD. The rapid degradation of glyphosate and AMPA indicate that good degradation can also be expected by chloramination as chlorine is generally dosed prior to ammonia and chlorine would thus have sufficient time to react with glyphosate and AMPA.

In the additional tests carried out in this work, the free Cl_2 concentration was relatively stable over the 30 min that the experiments lasted (Table 1). The results indicate that changes in pH had little influence on the degradation of glyphosate by chlorine; 96–100% was degraded in the three samples tested at 20 °C. The temperature had a larger influence on the glyphosate degradation with 71% being degraded at 5 °C compared to 96% at 20 °C. AMPA concentrations in samples from the glyphosate tests were all non-detectable, confirming the effective degradation of AMPA by chlorine.

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

- carboxylic acid carbon of glyphosate/glycine is converted to CO₂;
- C2 of glyphosate/glycine is converted to CO₂ and methanediol;
- C3 of glyphosate is converted to methanediol;

		pH Temp. (°C)	Free Cl ₂ residual (mg L ⁻¹)			Final conc.		
Compound spiked	рН		0 min	30 min	initial conc. (µg L ⁻¹)	Glyph. (μg L ⁻¹)	AMPA (µg L ⁻¹)	Removal (%)
Glyphosate	6.00	20.5	1.46	1.46	2.17	0.017	<0.016	99
Glyphosate	7.66	20.5	1.38	1.13	3.17	0.141	< 0.064	96
Glyphosate	8.60	20.5	1.46	1.38	2.17	0.007	< 0.016	>99
Glyphosate	7.52	4.9	1.38	1.28	3.17	0.915	< 0.064	71
Glyphosate	7.52	10.2	1.38	1.24	3.17	0.552	< 0.064	83
AMPA	6.25	20.5	1.42	1.28	3.65	N/A	< 0.016	>99
AMPA	7.08	20.5	1.46	1.31	3.65	N/A	< 0.016	>99
AMPA	8.38	20.5	1.51	1.42	3.65	N/A	< 0.016	>99
AMPA	8.38	6.2	1.56	1.46	3.65	N/A	< 0.016	>99
AMPA	8.38	9.8	1.56	1.46	3.65	N/A	< 0.016	>99

Table 1 Results of chlorination tests in this work

N/A = not analysed.

- 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 h 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 found that the reaction was fast with complete degradation when the first sample was taken after 10 min. Modelled results indicated 99% degradation after 5 seconds.

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 degrading glyphosate. Speth (1993) reported that the combined effect of chlorine dioxide and coagulation reduced the glyphosate concentration from 0.74 to 0.59 mg L^{-1} with a ClO₂ residual of 1.07 mg L^{-1} . After sedimentation (9 h contact time), the ClO₂ residual had reduced to 0.26 mg L^{-1} and glyphosate had reduced to 0.33 mg L^{-1} , achieving an overall reduction of 56%.

The results from the current work with ClO₂ as the oxidant are shown in Table 2. The degradation of glyphosate by ClO₂ was less effective than that for other oxidants, ranging from 17 to 93%. The highest degradation was seen for the low pH samples (\sim pH 6) with high temperature (22 °C) and high ClO₂ concentrations. The increased degradation as pH decreases could be due to changes in the speciation of glyphosate, rather than a direct influence on the oxidative potential of chlorine dioxide. Glyphosate has a second pKa of 5.44 (Sheals et al. 2002) and the results suggest that the singly deprotonated form of glyphosate $(-OOC-CH_2-NH_2^+-PO_3H^- \text{ or } H_2L^-)$ could potentially be more readily oxidised by ClO2 than the doubly deprotonated form ($^{-}OOC-CH_2-NH_2^+-PO_3^{2-}$ or HL^{2-}) that dominates between pH 5.44 and 10.13. At pH 6, the concentration of H_2L^- is about 30% of the total

			ciu ₂ residuai (mg t -)		hulfint name	Final conc.		
Compound pH T	Temp. (°C)	0 min	30 min	mmai conc. (μg L ⁻¹)	Glyph. (µg L ⁻¹)	AMPA (µg L ⁻¹)	Removal (%)	
Glyphosate	6.04	23	0.52	0.39	2.47	0.58	N/A	76
Glyphosate	7.96	23	0.39	0.20	2.47	1.35	N/A	45
Glyphosate	8.60	23	0.39	0.27	2.47	1.42	N/A	43
Glyphosate	8.05	5.2	1.35	1.35	2.47	1.64	N/A	34
Glyphosate	8.05	11.5	1.35	1.16	2.47	1.48	N/A	40
Glyphosate	6.05	21.1	1.23	1.03	2.17	0.16	0.097	93
Glyphosate	7.61	21.1	0.84	0.59	2.17	0.53	0.017	76
Glyphosate	8.56	21.1	1.10	1.03	2.17	0.53	0.093	76
Glyphosate	7.61	4.2	0.39	0.27	2.17	1.79	0.063	17
Glyphosate	7.61	11.6	0.91	0.84	2.17	1.16	0.039	46
AMPA	6.25	20.5	1.35	1.23	3.65	N/A	<0.016	>99
AMPA	7.08	20.5	1.03	0.39	3.65	N/A	< 0.016	>99
AMPA	8.38	20.5	1.35	1.16	3.65	N/A	< 0.016	>99
AMPA	8.38	6.2	1.42	1.10	3.65	N/A	< 0.016	>99
AMPA	8.38	10.8	1.35	1.16	3.65	N/A	< 0.016	>99

Table 2 Results of chlorine dioxide tests in this work

N/A = not analysed.

concentration of glyphosate, decreasing to about 1% at pH 7.5 and 0.1% at pH 8.5.

Low concentrations of AMPA were detected in the glyphosate test samples (1-5%) of total glyphosate concentration), suggesting that AMPA was formed as a degradation product when glyphosate was oxidised by ClO₂. However, for AMPA alone, complete degradation of AMPA was seen for all conditions tested, suggesting AMPA is readily degraded by ClO₂.

Ozone, UV and AOPs

The work reported in the literature suggests that better than 90% degradation of glyphosate and AMPA can be achieved with ozonation. Less degradation 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 and AMPA was small. Klinger et al. (2000) carried out tests with deionised water, which resulted in poor degradation of both glyphosate and AMPA. This may have been due to a low concentration of free radicals, particularly as degradation was greater at increased pH. In pilot plant tests, Speth (1993) reported that a dose of $1 \text{ mg } L^{-1}$ ozone degraded only 60% of glyphosate after 7 min contact time. Increased ozone doses of 1.9 and 2.9 mg L^{-1} gave complete degradation of glyphosate $(800-1,000 \ \mu g \ L^{-1})$. At the lowest ozone dose, the ozone demand of the water (including the contribution from the high glyphosate concentration) probably made insufficient ozone available to provide effective glyphosate degradation.

Hopman *et al.* (1995) reported that a dose of 0.8 mg L^{-1} ozone reduced 22 µg L⁻¹ glyphosate to below the LOD at a treatment works. Seven out of 10 measurements of AMPA showed between 25 and 77% reduction of AMPA; the remaining three measurements indicated an increase in AMPA after ozonation, suggesting production of AMPA from breakdown of glyphosate. 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. 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 may not be herbicide derived. 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 μ g L⁻¹ of AMPA and glyphosate, respectively. Ozonation with 10 min 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.

The results in the literature suggest that ozonation as applied in water treatment is highly effective for degradation of both glyphosate and AMPA. The ozonation treatment carried out in the current work degraded all of the glyphosate and AMPA to below the LOD after 15 min contact time (Table 3) and no temperature effect was seen. The initial O₃ concentration was similar between all of the tests and the O₃ demand increased with increasing temperature. Ozone was highly effective in degrading both glyphosate and AMPA and virtually complete degradation was achieved under the conditions tested. No AMPA was detected in any of the treated samples from the glyphosate tests.

A further set of tests was carried out with simultaneous use of O_3 and H_2O_2 , at 0.5 and 1.0 mg L⁻¹ (Table 4). The ozone concentrations quickly decreased indicating rapid breakdown of the ozone to produce hydroxyl radicals. The initial O₃ concentration was significantly lower in the presence of H_2O_2 due to the reaction between O_3 and H_2O_2 to generate hydroxyl radicals. The combination of O₃/H₂O₂ was as effective as O3 alone in degrading glyphosate and complete degradation was achieved under the conditions tested. In the sample from the glyphosate tests with the highest H_2O_2 concentration, traces of AMPA were found at <2% of total glyphosate concentration. With the addition of H₂O₂ the degradation of AMPA seems to decrease with an increasing H2O2 dose, although 85% was still degraded at the highest H₂O₂ concentration. This is in line with the results from the glyphosate tests, where AMPA was detected at the highest H_2O_2 concentration.

A limited amount of work has been carried out investigating the degradation of glyphosate using UV and

Table 3	Results	ot	ozonation	test	IN	this	work	
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		O3 residual (mg L ⁻¹)			Final conc.		
Compound spiked	Temp. (°C)	0 min	15 min	initial conc. (µg L ⁻¹)	Glyph. (µg L ⁻¹)	AMPA (µg L ⁻¹)	Removal (%)
Glyphosate	6.7	0.76	0.48	2.76	< 0.014	N/A	>99
Glyphosate	10.8	0.76	0.44	2.76	< 0.014	N/A	>99
Glyphosate	15.2	0.76	0.35	2.76	< 0.014	N/A	>99
Glyphosate	6.8	0.42	0.24	2.59	< 0.006	< 0.016	>99
Glyphosate	11.9	0.41	0.18	2.59	<0.006	< 0.016	>99
Glyphosate	15.0	0.41	0.19	2.59	< 0.006	< 0.016	>99
AMPA	5.1	0.51	0.16	3.65	N/A	< 0.016	>99
AMPA	10.5	0.54	0.10	3.65	N/A	< 0.016	>99
AMPA	13.4	0.55	0.10	3.65	N/A	< 0.016	>99

N/A = not analysed.

 Table 4
 Results of ozonation with hydrogen peroxide at 15 °C in this work

	H ₂ O ₂ dose (mg L ⁻¹)	O_3 residual (mg L ⁻¹)			Final conc.		
Compound spiked		0 min	15 min	Initial conc. (µg L ⁻¹)	Glyph. (µg L ⁻¹)	AMPA (µg L ⁻¹)	Removal (%)
Glyphosate	0.5	0.46	0.04	2.76	< 0.014	N/A	>99
Glyphosate	1.0	0.24	0.04	2.76	< 0.014	N/A	>99
Glyphosate	0.5	0.18	0.05	2.59	< 0.006	< 0.016	>99
Glyphosate	1.0	0.09	0.06	2.59	< 0.006	0.042	98
AMPA	0.5	0.16	0.02	3.65	N/A	0.11	97
AMPA	1.0	0.04	0.02	3.65	N/A	0.54	85

N/A = not analysed.

UV/H2O2. Lund-Høie & Friestad (1986) showed that an initial concentration of 1 mg L^{-1} was reduced by 50% after 4 days at 20 °C and a UV intensity of 30 W/cm² in deionised water. Manassero et al. (2010) showed that UV/H2O2 degraded 60% of the glyphosate (50 mg L^{-1}) after 5 h at 25 °C and that the treatment was more effective at neutral to alkaline pH values. The initial H2O2 concentration used was 75 mg L^{-1} for H_2O_2 but the UV dose was not stated. The degradation products found were non-toxic and it was suggested that complete mineralisation of glyphosate was not necessary to achieve non-toxic stable end-products. Bourgeois et al. (2012) suggested that a low-pressure UV lamp was more efficient than a medium-pressure lamp for degradation of 300 mg L⁻¹ of glyphosate but UV doses were not quoted. Significant amounts of by-products were reported but these were not identified or quantified.

Glyphosate is known to adsorb to TiO₂, with adsorption increasing with decreasing pH (Shifu & Yunzhang 2007; Muneer & Boxall 2008) and it is therefore hard to distinguish between removal and degradation in UV/TiO2 treatment. Shifu & Yunzhang (2007) studied the degradation of glyphosate in a UV/TiO₂ system in deionised water with 42 mg L^{-1} of glyphosate. The degradation of glyphosate increased up to 92% after 3.5 h illumination time and 4 mg L^{-1} of TiO₂, but the efficiency decreased when $>6 \text{ mg L}^{-1}$ of TiO₂ was used, as the increased concentration caused light scattering and screening effects. The pH dependency of degradation was relatively low; after 1 h illumination between 35 and 50% was degraded between pH 4 and 12. The degradation increased to 67% at pH 2. Muneer & Boxall (2008) studied the degradation of glyphosate (169 mg L^{-1}) using UV and TiO_2 (1 mg L⁻¹) but found the degradation more effective at alkaline pH; approximately 90% was degraded at pH 11 after 90 min compared to 40% at pH 3 and detected sarcosine and glycine as degradation products. Xue et al. (2011) showed that doping the TiO₂ with 0.15% Ce increased the degradation by 50% and >70% was degraded after 1 h UV illumination time with an initial concentration of 17 mg L^{-1} . Echavia *et al.* (2009) also used a combination of UV and TiO₂ and showed that complete removal could be achieved after 60 min at an initial glyphosate concentration of 17 mg L^{-1} . This removal did, however, also occur in the dark and was attributed to the adsorption of glyphosate to the TiO₂ surface. Assalin et al. (2009) reported >99% degradation of glyphosate at pH 6.5 after 30 min UV illumination time with 0.1 g/L of TiO₂ and an initial glyphosate concentration of 42 mg L^{-1} . Removal by adsorption had, however, not been accounted for and AMPA was found as a degradation product. Glyphosate can also be degraded using the Fenton reaction; Chen et al. (2007) reported >60% removal at pH 3.5 with initial concentrations of glyphosate of 5 mg L^{-1} , Fe³⁺ of 20 μ M and oxalate of 300 μ M.

The glyphosate concentrations used in the reviewed works investigating the degradation of glyphosate using

UV techniques are orders of magnitudes higher than what can be expected at water treatment works but the results indicate that significant degradation could be achieved by the combination of UV and H_2O_2 , although from the ozone/peroxide results of this work (see above), the degradation of AMPA may be less effective by hydroxyl radicals.

The use of UV, O₃ and AOPs was further investigated in this work by the use of a flow through pilot reactor. The tap water used had a temperature of 22 °C, pH between 7 and 7.2, alkalinity between 215 and 219 mg L⁻¹ CaCO₃, and a UV transmittance of 96.7–96.8%. Measured concentrations of both glyphosate and AMPA were less than the target $3 \mu g L^{-1}$ (Table 5) and AMPA was present in the glyphosate stock solution. It has not been determined whether this was a result of decomposition in solution, or AMPA being present in the original glyphosate product. However, it does not impact on the quality of the results, as the test concentrations were high enough to provide reliable data, and were representative of those found in source waters.

The UV dose used in drinking water treatment is typically in the region of $40-100 \text{ mJ cm}^{-2}$ when used for disinfection alone (US EPA 2006; Bolton & Cotton 2008).

Minut name

		Initial ages	rmai conc.		
Compound spiked	Operating conditions	initial conc. (µg L ⁻¹)	Glyph. (µg L ⁻¹)	AMPA (µg L ⁻¹)	Removal (%)
Glyphosate	Feed water	1.72	1.72	0.30	0
Glyphosate	$UV 740 \text{ mJ cm}^{-2}$	1.72	1.29	0.34	25
Glyphosate	UV 1,240 mJ cm $^{-2}$	1.72	1.10	0.42	36
Glyphosate	UV 740 mJ cm ⁻² , H_2O_2 5 mg L^{-1}	1.72	0.21	0.59	88
Glyphosate	UV 1,240 mJ cm ⁻² , H_2O_2 5 mg L^{-1}	1.72	0.15	0.69	91
Glyphosate	$O_3 2 \text{ mg L}^{-1}$	1.72	0.068	0.17	96
Glyphosate	$O_3 \ 2 \ mg \ L^{-1}, \ H_2 O_2 \ 2 \ mg \ L^{-1}$	1.72	< 0.006	0.22	99
AMPA	Feed water	2.31	N/A	2.31	0
AMPA	UV 740 mJ cm^{-2}	2.31	N/A	2.16	6
AMPA	UV 1,240 mJ cm $^{-2}$	2.31	N/A	1.57	32
AMPA	UV 740 mJ cm ⁻² , H_2O_2 5 mg L ⁻¹	2.31	N/A	2.13	8
AMPA	UV 1,240 mJ cm ⁻² , H_2O_2 5 mg L^{-1}	2.31	N/A	1.18	49
AMPA	$O_3 \ 2 \ mg \ L^{-1} \ 1 \ min \ contact \ time$	2.31	N/A	0.86	63
AMPA	$O_3 \ 2 \ mg \ L^{-1} \ 10 \ min \ contact \ time$	2.31	N/A	< 0.016	>99
	$O_3 \ 2 \ mg \ L^{-1}, \ H_2O_2 \ 2 \ mg \ L^{-1}$	2.31	N/A	1.50	35

Table 5 | Results of UV, O3 and AOP tests for glyphosate and AMPA removal in this work

N/A = not analysed.

Doses >1,000 mJ cm⁻² are usually required for >50% degradation of organic micropollutants (e.g. Ijpelaar *et al.* 2002; Kruithof *et al.* 2007). The doses used in this work were 740 and 1,240 mJ cm⁻² and this resulted in a degradation of 36% of the spiked glyphosate for the highest dose (Table 5). The addition of 5 mg L⁻¹ of H₂O₂ significantly increased the degradation of glyphosate to 88–91% using the same UV doses, while the AMPA concentration increased. This indicates that AMPA is not readily degraded by UV or UV/H₂O₂ at the conditions used. The ozonation tests were run with 1 min contact time (Table 5) and confirmed the evidence of rapid degradation of glyphosate from previous tests. The AMPA concentration also decreased in the ozonation tests.

Repeating the tests in the flow through system with AMPA it was confirmed that AMPA is poorly degraded by UV and UV/H₂O₂ under the conditions tested; between 6 and 36% was removed at the doses used (Table 5). The results from the ozonation tests showed lower degradation of AMPA (35–66%) than the previous results for 15 min contact time (>99%). This was due to the shorter contact time of 1 min as the degradation increased to >99% when the contact time in the flow through pilot plant was increased to 10 min. The results also confirmed the previous finding that the degradation of AMPA in the O₃/H₂O₂ system was reduced compared to the O₃ only system.

The work reported here has used H_2O_2 concentrations between 0.5 and 5 mg L⁻¹, which are, based on our experience, typical concentrations used by UK water utilities. No attempts have been made to optimise the O_3/H_2O_2 and UV/H_2O_2 ratios and the degradation could potentially be increased by increasing the H_2O_2 dose, especially in the UV/H_2O_2 system. This would, however, also increase the treatment cost, making the treatment prohibitively expensive, especially since there are less costly alternatives available.

Activated carbon

Glyphosate is reported to have a log K_{ow} (octanol:water partition coefficient) of -4.00 (SRC 2012). This indicates high water solubility and an expectation of limited adsorption by activated carbon. The compound may be more amenable to removal through the development of biological activity in GAC (granular activated carbon), although the mechanism may depend strongly on adsorption of the compounds first to allow effective biodegradation.

The results from Speth (1993) in distilled water indicate that glyphosate would be amenable to adsorption by GAC. However, Speth (1993) also reports results for tests carried out in river water which were consistent with the relatively poor removal seen in other work. The presence of competing organic matter would be expected to reduce the capacity of the GAC to adsorb glyphosate or AMPA. Lange & Post (2000) reported an average removal of 21% of AMPA by GAC, for a pre-treated surface water (coagulation and rapid gravity filtration) but less than 10% removal for glyphosate. The results for AMPA show removal decreasing quickly to <40% after a specific throughput of 2 m³ kg⁻¹ and <20%after 9 m³ kg⁻¹. This represents effective operation for only a week or two, despite low influent concentrations of $0.06 \,\mu g \, L^{-1}$ glyphosate and $0.25 \,\mu g \, l^{-1}$ AMPA. Hopman et al. (1995) found that at one site in the Netherlands, GAC with an operational time of 22 months reduced an AMPA influent concentration of 0.33 to $0.04 \,\mu g \, L^{-1}$. 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 $1 \text{ ug } \text{L}^{-1}$. The removal only lasted a few days and suggests that GAC would not offer a practical treatment strategy. No published information was found on the use of PAC for removal of glyphosate or AMPA.

The removal of glyphosate and AMPA by PAC was further investigated in this work (Table 6). Although the results are somewhat scattered, it is clear the PAC was ineffective as a removal treatment for glyphosate, even at the relatively high dose for water treatment of 25 mg L⁻¹ no more than 20% was removed. This is not surprising considering the high water solubility (approximately 10 g L⁻¹) and low log K_{ow} for glyphosate. No major differences between the different PACs can be seen.

The tap water used for the PAC testing had not been thoroughly de-chlorinated, and the initial concentration of AMPA is therefore lower than expected (Table 6). However, PAC removes Cl_2 and this stops the degradation of AMPA by Cl_2 . This explains why the removal of AMPA seems to increase with decreasing PAC dose. The removal that actually occurs is degradation by Cl_2 and an increased PAC dose removes more Cl_2 . A similar, though much less

			Initial conc.	Final conc.	
Compound	PAC	PAC conc. (mg L ⁻¹)	(µg L ⁻¹)	(μg L ⁻¹)	
Glyphosate	Norit W35	5.1	3.13	2.51	20
Glyphosate	Norit W35	15.2	3.13	2.76	12
Glyphosate	Norit W35	25.3	3.13	3.14	0
Glyphosate	Norit SA Super	5.2	3.13	2.86	9
Glyphosate	Norit SA Super	15.0	3.13	2.46	22
Glyphosate	Norit SA Super	25.0	3.13	3.03	3
Glyphosate	Chemviron W	5.1	3.13	2.57	18
Glyphosate	Chemviron W	15.1	3.13	2.79	11
Glyphosate	Chemviron W	25.2	3.13	2.72	13
AMPA	Norit W35	5.1	1.57ª	1.09	31
AMPA	Norit W35	15.2	1.57^{a}	1.39	12
AMPA	Norit W35	25.3	1.57 ^a	2.19	0
AMPA	Norit SA Super	5.2	1.57 ^a	1.92	0
AMPA	Norit SA Super	15.0	1.57 ^a	2.28	0
AMPA	Norit SA Super	25.0	1.57 ^a	3.23	0
AMPA	Chemviron W	5.1	1.57^{a}	1.63	0
AMPA	Chemviron W	15.1	1.57ª	1.49	5
AMPA	Chemviron W	25.2	1.57 ^a	1.92	0

Table 6 Results of PAC tests for glyphosate removal in this work

^aSpiked at $3 \mu g L^{-1}$.

marked, effect is suggested for glyphosate. The conclusion is that the PACs investigated would not provide adequate removal of glyphosate and AMPA.

Pressure driven membrane processes

Roche *et al.* (2004) carried out laboratory tests with nanofiltration (NF) on a group of seven pesticides, including AMPA and glyphosate. Distilled water spiked with $2 \ \mu g \ L^{-1}$ AMPA and glyphosate and 500 mg L^{-1} CaCl₂ (pH 7, temperature 25 °C) was tested at a flux of 20 L h m⁻². The retention (i.e. removal) of glyphosate and AMPA was >95% after 72 hours. Saitúa *et al.* (2012) showed that NF could remove >85% of glyphosate at initial concentrations up to 250 mg L^{-1} and the removal increased as the pH increased. Hopman *et al.* (1995) tested four low pressure 'hyper filtration' (reverse osmosis, RO) membranes in a pilot plant and these were able to reduce glyphosate concentrations of 4.5 μ g L^{-1} to below the LOD. Speth (1993) evaluated the removal of glyphosate through ultrafiltration (UF) membranes with a molecular weight cut-off (MWC) of 100,000, 1000 and 500. The experiments showed that glyphosate was not removed from surface water by 100,000 MWC membranes. The 1000 MWC membranes initially removed 50% of the glyphosate and the 500 MWC membranes initially removed all glyphosate. Whilst NF and RO have been shown to remove glyphosate and AMPA, large scale production of water by these methods is expensive, not commonly used and unlikely to be adopted for removal of organic micropollutants. Some removal by UF 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.

Air stripping

The Henry's Law Constant for glyphosate, 4.08×10^{-19} atm m³ M⁻¹ (SRC 2012) indicates that it would not be amenable to removal by air stripping.

Table 7 Summary of removal of glyphosate and AMPA

Treatment process	Glyphosate removal (%)	AMPA removal (%)		
Bank and dune filtration	20-50	25-95		
Aluminium coagulant and clarification	15–40 Not a reliable barrier for glypho	20–25 osate and AMPA		
Iron coagulant and clarification	40–70 Not a reliable barrier for glypho	20–85 Disate and AMPA		
Slow sand filtration	The limited information suggest but removal is likely to be hig	s that significant removal can be achieved shly dependent on conditions		
Chlorination	74– >99 Likely to provide the main barr	40– >95 ier at most water treatment works		
Chlorine dioxide	 >99 Removal of glyphosate is variable and works best at lower pH and high temperature. Good removal of AMPA can be expected 			
Ozonation	60->99 25-95 Provides an additional barrier at works where already installed for othe pesticides and micropollutants			
UV irradiation	Not effective alone at doses use	d in water treatment		
Advanced oxidation	O ₃ /H ₂ O ₂ provides an additional barrier at works where already installed. UV/H ₂ O ₂ show good removal of glyphosate but not AMPA UV/TiO ₂ can degrade significant amounts of both compounds but irradiation times are long			
Activated carbon adsorption	10–90 20–70 Higher removals relate to virgin GAC and are unlikely to be achieved under practical conditions. Not a reliable barrier			
Membrane filtration	>90 (NF/RO) >50 (UF) ^a Membrane processes not widely be installed solely as a barrier	>95 (NF/RO) No information found for UF y used in water treatment, and unlikely to r to pesticides		
Air stripping	Not expected to be effective based on chemical characteristics			

^aDepending on membrane type.

CONCLUSIONS

The review and laboratory tests have shown that glyphosate and AMPA are both readily degraded or removed by a number of common treatment steps at drinking water treatment plants, as summarised in Table 7. Biodegradation and adsorption processes can be highly effective in degrading or removing glyphosate and AMPA in bank filtration and SSF. These processes could potentially be of importance in biologically active GAC but the residence time is generally much shorter. Iron-based coagulants are generally more effective than Al-based coagulants in removing glyphosate and AMPA; coagulation is particularly effective if coagulant residuals are removed by filtration. Ozonation and chlorination are highly effective in degrading both glyphosate and AMPA but a decrease in temperature reduces the efficiency. Combining O_3 and H_2O_2 did not improve the degradation compared to O_3 alone; in fact a decrease was observed at high H_2O_2 concentrations. UV doses typically used for disinfection will not degrade significant amounts of either compound. Higher UV doses in combination with H_2O_2 showed good degradation of glyphosate but not AMPA. Chlorine dioxide is effective for glyphosate and AMPA degradation at around pH 6 but the efficiency decreases with increasing pH and decreasing temperature. UV/TiO₂ treatment can degrade significant amounts of glyphosate but the irradiation time needed is long. Ultrafiltration, NF and RO can also be effective in removing glyphosate and AMPA but the cut-off for UF need careful consideration. Activated carbon is not likely to provide a practical removal option for either compound.

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