

## 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  $>0.1 \mu\text{g L}^{-1}$ . 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  $\text{Cl}_2$  and  $\text{O}_3$ , 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 and AMPA degradation but the combination of UV/ $\text{H}_2\text{O}_2$  provided significant degradation of glyphosate, but not AMPA, under the conditions investigated. UV/ $\text{TiO}_2$  treatment can degrade significant amounts of glyphosate but the irradiation time needed is long. Removal or degradation by bank filtration, slow sand filtration,  $\text{ClO}_2$  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,  $\text{H}_2\text{O}_3\text{P-CH}_2\text{-NH-CH}_2\text{-COOH}$ ) 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  $0.1 \mu\text{g L}^{-1}$  for individual pesticides, their relevant metabolites, decay and reaction products and  $0.5 \mu\text{g L}^{-1}$  for

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  $700 \mu\text{g L}^{-1}$  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,  $\text{H}_2\text{O}_3\text{P-CH}_2\text{-NH}_2$ ) 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

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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  $0.1 \mu\text{g L}^{-1}$  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  $\text{O}_3$ , UV,  $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$ . 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  $\text{Cl}_2$ ,  $\text{ClO}_2$ ,  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , 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  $3 \mu\text{g L}^{-1}$  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  $0.2\text{--}0.4 \text{ mg O}_3 \text{ L}^{-1}$  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  $\text{O}_3$  generator (Labo II ozonator from Ozotech Ltd) and a bubble diffuser stone. Following ozonation, the  $\text{O}_3$  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  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , at 0.5 and  $1.0 \text{ mg L}^{-1}$  of  $\text{H}_2\text{O}_2$ . The ozonation conditions were identical to the test with  $\text{O}_3$  alone. At the end of the contact period, the residual  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  were quenched with sodium thiosulphate as above.

For the chlorine tests, 1 L samples of the spiked water were dosed with sodium hypochlorite at  $1.5 \text{ mg Cl}_2 \text{ L}^{-1}$ . The dosed water was left for 30 min at the desired temperature. At the end of the contact period, the residual  $\text{Cl}_2$  was measured and then quenched with sodium thiosulphate as above. The tests with  $\text{Cl}_2$  were repeated but with  $\text{ClO}_2$  as the oxidant. The  $\text{ClO}_2$  was added as crushed tablets (Accepta). The initial target concentration of  $\text{ClO}_2$  was  $1 \text{ mg L}^{-1}$ .

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  $25 \text{ mg L}^{-1}$ . 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/ $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , and UV/ $\text{O}_3/\text{H}_2\text{O}_2$  were investigated in a flow through pilot reactor from ITT Wedeco, consisting of in-line  $\text{H}_2\text{O}_2$  dosing,  $\text{O}_3$  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<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> can then be set independently. Two tests were performed, each with the same matrix of operating conditions. The feed tank was filled with 2 m<sup>3</sup> 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<sup>-1</sup> and the water recirculated to ensure the compound was evenly distributed.

The concentrations of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub> and ClO<sub>2</sub> 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 9-fluorenylmethyl 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 µg/L was 99% with a LOD of 0.006 µg/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 µg L<sup>-1</sup> in the river to 0.06 µg L<sup>-1</sup> 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 µg L<sup>-1</sup>). Ijpelaar *et al.* (2000) reported concentrations of up to 0.49 µg L<sup>-1</sup> glyphosate and 5.4 µg L<sup>-1</sup> 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 µg g<sup>-1</sup>.

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 µg L<sup>-1</sup>) 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  $5 \mu\text{g L}^{-1}$  for glyphosate and AMPA, respectively. Lange & Post (2000) reported that the raw water concentration ( $0.1 \mu\text{g L}^{-1}$  glyphosate and  $0.32 \mu\text{g L}^{-1}$  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  $1.8\text{--}3.3 \mu\text{g L}^{-1}$ . 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  $\text{pH} > 7$  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. Roche *et al.* (2004) studied the removal of glyphosate and AMPA by coagulation, using a surface water spiked with glyphosate ( $1 \mu\text{g L}^{-1}$ ). Either aluminium polychlorosulphate (WAC,  $30 \text{ mg L}^{-1}$ ) or ferric chloride ( $30\text{--}70 \text{ mg L}^{-1}$ ) 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  $0.48 \mu\text{g L}^{-1}$ , to  $<0.05 \mu\text{g L}^{-1}$  ( $>80\%$  removal). Schlett *et al.* (2005) studied the effect of SSF where the inlet water contained  $<0.05\text{--}0.19 \mu\text{g L}^{-1}$  glyphosate, reducing to  $<0.08 \mu\text{g L}^{-1}$  after filtration. The concentration of AMPA was in the range  $<0.08\text{--}0.7 \mu\text{g L}^{-1}$  at the inlet, and was reduced to  $<0.08 \mu\text{g L}^{-1}$  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 ( $0.2\text{--}0.6 \text{ mg L}^{-1}$  chlorine), between 40 and 100% of AMPA was degraded for initial concentrations of  $0.2\text{--}5 \mu\text{g L}^{-1}$ . A chlorine dose of  $2 \text{ mg L}^{-1}$  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  $\mu\text{g L}^{-1}$  of glyphosate. With an applied chlorine dose of 2.1  $\text{mg L}^{-1}$ , the glyphosate concentration was reduced below the LOD (25  $\mu\text{g L}^{-1}$ ) 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  $\mu\text{g L}^{-1}$  glyphosate was found to be completely degraded by a chlorine dose of 2  $\text{mg L}^{-1}$ , after a contact time of 20 min, and 0.56  $\mu\text{g L}^{-1}$  AMPA was degraded for the same conditions. A concentration of 5  $\mu\text{g L}^{-1}$  glyphosate was degraded by a chlorine dose of 0.75  $\text{mg L}^{-1}$ , after a contact time of 4 hours, and 0.42  $\mu\text{g L}^{-1}$  AMPA was degraded under the same conditions. After a contact time of 120 seconds, 11.5  $\mu\text{g L}^{-1}$  glyphosate and 0.14  $\mu\text{g L}^{-1}$  AMPA were completely degraded, indicating fast kinetics. Lange & Post (2000) found that a chlorine concentration of 0.08  $\text{mg L}^{-1}$   $\text{Cl}_2$  achieved 74 and 80% degradation of glyphosate and AMPA respectively, for a drinking water spiked at 0.05–0.4  $\mu\text{g L}^{-1}$ , after a contact time of 5 min. A chlorine dose of 0.40  $\text{mg L}^{-1}$  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  $\text{Cl}_2$  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  $\text{CO}_2$ ;
- C2 of glyphosate/glycine is converted to  $\text{CO}_2$  and methanediol;
- C3 of glyphosate is converted to methanediol;

**Table 1** | Results of chlorination tests in this work

Compound spiked	pH	Temp. (°C)	Free $\text{Cl}_2$ residual ( $\text{mg L}^{-1}$ )		Initial conc. ( $\mu\text{g L}^{-1}$ )	Final conc.		Removal (%)
			0 min	30 min		Glyph. ( $\mu\text{g L}^{-1}$ )	AMPA ( $\mu\text{g L}^{-1}$ )	
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

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<sup>-1</sup> with a ClO<sub>2</sub> residual of 1.07 mg L<sup>-1</sup>. After sedimentation (9 h contact time), the ClO<sub>2</sub> residual had reduced to 0.26 mg L<sup>-1</sup> and glyphosate had reduced to 0.33 mg L<sup>-1</sup>, achieving an overall reduction of 56%.

The results from the current work with ClO<sub>2</sub> as the oxidant are shown in Table 2. The degradation of glyphosate by ClO<sub>2</sub> was less effective than that for other oxidants, ranging from 17 to 93%. The highest degradation was seen for the low pH samples (~pH 6) with high temperature (22 °C) and high ClO<sub>2</sub> 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 pK<sub>a</sub> of 5.44 (Sheals *et al.* 2002) and the results suggest that the singly deprotonated form of glyphosate (<sup>-</sup>OOC-CH<sub>2</sub>-NH<sub>2</sub><sup>+</sup>-PO<sub>3</sub>H<sup>-</sup> or H<sub>2</sub>L<sup>-</sup>) could potentially be more readily oxidised by ClO<sub>2</sub> than the doubly deprotonated form (<sup>-</sup>OOC-CH<sub>2</sub>-NH<sub>2</sub><sup>+</sup>-PO<sub>3</sub><sup>2-</sup> or HL<sup>2-</sup>) that dominates between pH 5.44 and 10.13. At pH 6, the concentration of H<sub>2</sub>L<sup>-</sup> is about 30% of the total

Table 2 | Results of chlorine dioxide tests in this work

Compound	pH	Temp. (°C)	ClO <sub>2</sub> residual (mg L <sup>-1</sup> )		Initial conc. (µg L <sup>-1</sup> )	Final conc.		Removal (%)
			0 min	30 min		Glyph. (µg L <sup>-1</sup> )	AMPA (µg L <sup>-1</sup> )	
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

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  $\text{ClO}_2$ . However, for AMPA alone, complete degradation of AMPA was seen for all conditions tested, suggesting AMPA is readily degraded by  $\text{ClO}_2$ .

### 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  $2.9 \text{ mg L}^{-1}$  gave complete degradation of glyphosate ( $800\text{--}1,000 \text{ }\mu\text{g L}^{-1}$ ). 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  $0.8 \text{ mg L}^{-1}$  ozone reduced  $22 \text{ }\mu\text{g L}^{-1}$  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  $3 \text{ mg L}^{-1}$  using water with dissolved organic carbon concentration of  $0.6$  and  $2.0 \text{ mg L}^{-1}$ , spiked with  $1.1$  and  $1.8 \text{ }\mu\text{g L}^{-1}$  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  $\text{O}_3$  concentration was similar between all of the tests and the  $\text{O}_3$  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  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , at  $0.5$  and  $1.0 \text{ mg L}^{-1}$  (Table 4). The ozone concentrations quickly decreased indicating rapid breakdown of the ozone to produce hydroxyl radicals. The initial  $\text{O}_3$  concentration was significantly lower in the presence of  $\text{H}_2\text{O}_2$  due to the reaction between  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  to generate hydroxyl radicals. The combination of  $\text{O}_3/\text{H}_2\text{O}_2$  was as effective as  $\text{O}_3$  alone in degrading glyphosate and complete degradation was achieved under the conditions tested. In the sample from the glyphosate tests with the highest  $\text{H}_2\text{O}_2$  concentration, traces of AMPA were found at  $<2\%$  of total glyphosate concentration. With the addition of  $\text{H}_2\text{O}_2$  the degradation of AMPA seems to decrease with an increasing  $\text{H}_2\text{O}_2$  dose, although  $85\%$  was still degraded at the highest  $\text{H}_2\text{O}_2$  concentration. This is in line with the results from the glyphosate tests, where AMPA was detected at the highest  $\text{H}_2\text{O}_2$  concentration.

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

**Table 3** | Results of ozonation test in this work

Compound spiked	Temp. (°C)	O <sub>3</sub> residual (mg L <sup>-1</sup> )		Initial conc. (µg L <sup>-1</sup> )	Final conc.		Removal (%)
		0 min	15 min		Glyph. (µg L <sup>-1</sup> )	AMPA (µg L <sup>-1</sup> )	
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

Compound spiked	H <sub>2</sub> O <sub>2</sub> dose (mg L <sup>-1</sup> )	O <sub>3</sub> residual (mg L <sup>-1</sup> )		Initial conc. (µg L <sup>-1</sup> )	Final conc.		Removal (%)
		0 min	15 min		Glyph. (µg L <sup>-1</sup> )	AMPA (µg L <sup>-1</sup> )	
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/H<sub>2</sub>O<sub>2</sub>. Lund-Høie & Friestad (1986) showed that an initial concentration of 1 mg L<sup>-1</sup> was reduced by 50% after 4 days at 20 °C and a UV intensity of 30 W/cm<sup>2</sup> in deionised water. Manassero *et al.* (2010) showed that UV/H<sub>2</sub>O<sub>2</sub> degraded 60% of the glyphosate (50 mg L<sup>-1</sup>) after 5 h at 25 °C and that the treatment was more effective at neutral to alkaline pH values. The initial H<sub>2</sub>O<sub>2</sub> concentration used was 75 mg L<sup>-1</sup> for H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup> 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 TiO<sub>2</sub>, 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/TiO<sub>2</sub> treatment. Shifu & Yunzhang (2007) studied the degradation of glyphosate in a UV/TiO<sub>2</sub> system in deionised water with 42 mg L<sup>-1</sup> of glyphosate. The degradation of glyphosate increased up to 92% after 3.5 h illumination time and 4 mg L<sup>-1</sup> of TiO<sub>2</sub>, but the efficiency decreased when >6 mg L<sup>-1</sup> of TiO<sub>2</sub> 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<sup>-1</sup>) using UV and TiO<sub>2</sub> (1 mg L<sup>-1</sup>) 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 TiO<sub>2</sub> 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<sup>-1</sup>. *Echavia et al.* (2009) also used a combination of UV and TiO<sub>2</sub> and showed that complete removal could be achieved after 60 min at an initial glyphosate concentration of 17 mg L<sup>-1</sup>. This removal did, however, also occur in the dark and was attributed to the adsorption of glyphosate to the TiO<sub>2</sub> 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 TiO<sub>2</sub> and an initial glyphosate concentration of 42 mg L<sup>-1</sup>. 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<sup>-1</sup>, Fe<sup>3+</sup> of 20 μM and oxalate of 300 μM.

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<sub>2</sub>O<sub>2</sub>, 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, O<sub>3</sub> 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<sup>-1</sup> CaCO<sub>3</sub>, and a UV transmittance of 96.7–96.8%. Measured concentrations of both glyphosate and AMPA were less than the target 3 μg L<sup>-1</sup> (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 mJ cm<sup>-2</sup> when used for disinfection alone (US EPA 2006; Bolton & Cotton 2008).

**Table 5** | Results of UV, O<sub>3</sub> and AOP tests for glyphosate and AMPA removal in this work

Compound spiked	Operating conditions	Initial conc. (μg L <sup>-1</sup> )	Final conc.		Removal (%)
			Glyph. (μg L <sup>-1</sup> )	AMPA (μg L <sup>-1</sup> )	
Glyphosate	Feed water	1.72	1.72	0.30	0
Glyphosate	UV 740 mJ cm <sup>-2</sup>	1.72	1.29	0.34	25
Glyphosate	UV 1,240 mJ cm <sup>-2</sup>	1.72	1.10	0.42	36
Glyphosate	UV 740 mJ cm <sup>-2</sup> , H <sub>2</sub> O <sub>2</sub> 5 mg L <sup>-1</sup>	1.72	0.21	0.59	88
Glyphosate	UV 1,240 mJ cm <sup>-2</sup> , H <sub>2</sub> O <sub>2</sub> 5 mg L <sup>-1</sup>	1.72	0.15	0.69	91
Glyphosate	O <sub>3</sub> 2 mg L <sup>-1</sup>	1.72	0.068	0.17	96
Glyphosate	O <sub>3</sub> 2 mg L <sup>-1</sup> , H <sub>2</sub> O <sub>2</sub> 2 mg L <sup>-1</sup>	1.72	<0.006	0.22	99
AMPA	Feed water	2.31	N/A	2.31	0
AMPA	UV 740 mJ cm <sup>-2</sup>	2.31	N/A	2.16	6
AMPA	UV 1,240 mJ cm <sup>-2</sup>	2.31	N/A	1.57	32
AMPA	UV 740 mJ cm <sup>-2</sup> , H <sub>2</sub> O <sub>2</sub> 5 mg L <sup>-1</sup>	2.31	N/A	2.13	8
AMPA	UV 1,240 mJ cm <sup>-2</sup> , H <sub>2</sub> O <sub>2</sub> 5 mg L <sup>-1</sup>	2.31	N/A	1.18	49
AMPA	O <sub>3</sub> 2 mg L <sup>-1</sup> 1 min contact time	2.31	N/A	0.86	63
AMPA	O <sub>3</sub> 2 mg L <sup>-1</sup> 10 min contact time	2.31	N/A	<0.016	>99
AMPA	O <sub>3</sub> 2 mg L <sup>-1</sup> , H <sub>2</sub> O <sub>2</sub> 2 mg L <sup>-1</sup>	2.31	N/A	1.50	35

N/A = not analysed.

Doses  $>1,000 \text{ mJ cm}^{-2}$  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  $1,240 \text{ mJ cm}^{-2}$  and this resulted in a degradation of 36% of the spiked glyphosate for the highest dose (Table 5). The addition of  $5 \text{ mg L}^{-1}$  of  $\text{H}_2\text{O}_2$  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/ $\text{H}_2\text{O}_2$  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/ $\text{H}_2\text{O}_2$  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  $\text{O}_3/\text{H}_2\text{O}_2$  system was reduced compared to the  $\text{O}_3$  only system.

The work reported here has used  $\text{H}_2\text{O}_2$  concentrations between  $0.5$  and  $5 \text{ mg L}^{-1}$ , which are, based on our experience, typical concentrations used by UK water utilities. No attempts have been made to optimise the  $\text{O}_3/\text{H}_2\text{O}_2$  and UV/ $\text{H}_2\text{O}_2$  ratios and the degradation could potentially be increased by increasing the  $\text{H}_2\text{O}_2$  dose, especially in the UV/ $\text{H}_2\text{O}_2$  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  $2 \text{ m}^3 \text{ kg}^{-1}$  and  $<20\%$  after  $9 \text{ m}^3 \text{ kg}^{-1}$ . This represents effective operation for only a week or two, despite low influent concentrations of  $0.06 \text{ } \mu\text{g L}^{-1}$  glyphosate and  $0.25 \text{ } \mu\text{g L}^{-1}$  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  $0.04 \text{ } \mu\text{g L}^{-1}$ . 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  $1 \text{ } \mu\text{g L}^{-1}$ . 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  $25 \text{ mg L}^{-1}$  no more than 20% was removed. This is not surprising considering the high water solubility (approximately  $10 \text{ g L}^{-1}$ ) 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  $\text{Cl}_2$  and this stops the degradation of AMPA by  $\text{Cl}_2$ . This explains why the removal of AMPA seems to increase with decreasing PAC dose. The removal that actually occurs is degradation by  $\text{Cl}_2$  and an increased PAC dose removes more  $\text{Cl}_2$ . A similar, though much less

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

Compound	PAC	PAC conc. (mg L <sup>-1</sup> )	Initial conc.	Final conc.	Removal (%)
			(µg L <sup>-1</sup> )		
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	1.57 <sup>a</sup>	1.09	31
AMPA	Norit W35	15.2	1.57 <sup>a</sup>	1.39	12
AMPA	Norit W35	25.3	1.57 <sup>a</sup>	2.19	0
AMPA	Norit SA Super	5.2	1.57 <sup>a</sup>	1.92	0
AMPA	Norit SA Super	15.0	1.57 <sup>a</sup>	2.28	0
AMPA	Norit SA Super	25.0	1.57 <sup>a</sup>	3.23	0
AMPA	Chemviron W	5.1	1.57 <sup>a</sup>	1.63	0
AMPA	Chemviron W	15.1	1.57 <sup>a</sup>	1.49	5
AMPA	Chemviron W	25.2	1.57 <sup>a</sup>	1.92	0

<sup>a</sup>Spiked at 3 µg L<sup>-1</sup>.

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 µg L<sup>-1</sup> AMPA and glyphosate and 500 mg L<sup>-1</sup> CaCl<sub>2</sub> (pH 7, temperature 25 °C) was tested at a flux of 20 L h m<sup>-2</sup>. 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<sup>-1</sup> 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 µg L<sup>-1</sup> 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<sup>-19</sup> atm m<sup>3</sup> M<sup>-1</sup> (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 glyphosate and AMPA	20–25
Iron coagulant and clarification	40–70 Not a reliable barrier for glyphosate and AMPA	20–85
Slow sand filtration	The limited information suggests that significant removal can be achieved but removal is likely to be highly dependent on conditions	
Chlorination	74–>99 Likely to provide the main barrier at most water treatment works	40–>95
Chlorine dioxide	17–93 Removal of glyphosate is variable and works best at lower pH and high temperature. Good removal of AMPA can be expected	>99
Ozonation	60–>99 Provides an additional barrier at works where already installed for other pesticides and micropollutants	25–95
UV irradiation	Not effective alone at doses used in water treatment	
Advanced oxidation	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> provides an additional barrier at works where already installed. UV/H <sub>2</sub> O <sub>2</sub> show good removal of glyphosate but not AMPA UV/TiO <sub>2</sub> can degrade significant amounts of both compounds but irradiation times are long	
Activated carbon adsorption	10–90 Higher removals relate to virgin GAC and are unlikely to be achieved under practical conditions. Not a reliable barrier	20–70
Membrane filtration	>90 (NF/RO) >50 (UF) <sup>a</sup> Membrane processes not widely used in water treatment, and unlikely to be installed solely as a barrier to pesticides	>95 (NF/RO) No information found for UF
Air stripping	Not expected to be effective based on chemical characteristics	

<sup>a</sup>Depending 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<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> did not improve the degradation compared to O<sub>3</sub> alone; in fact a decrease was observed at high H<sub>2</sub>O<sub>2</sub> concentrations. UV doses typically used for disinfection will not degrade significant amounts of either compound. Higher UV doses in combination with H<sub>2</sub>O<sub>2</sub> 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/TiO<sub>2</sub> 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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