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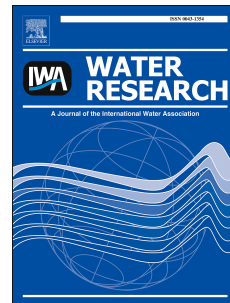
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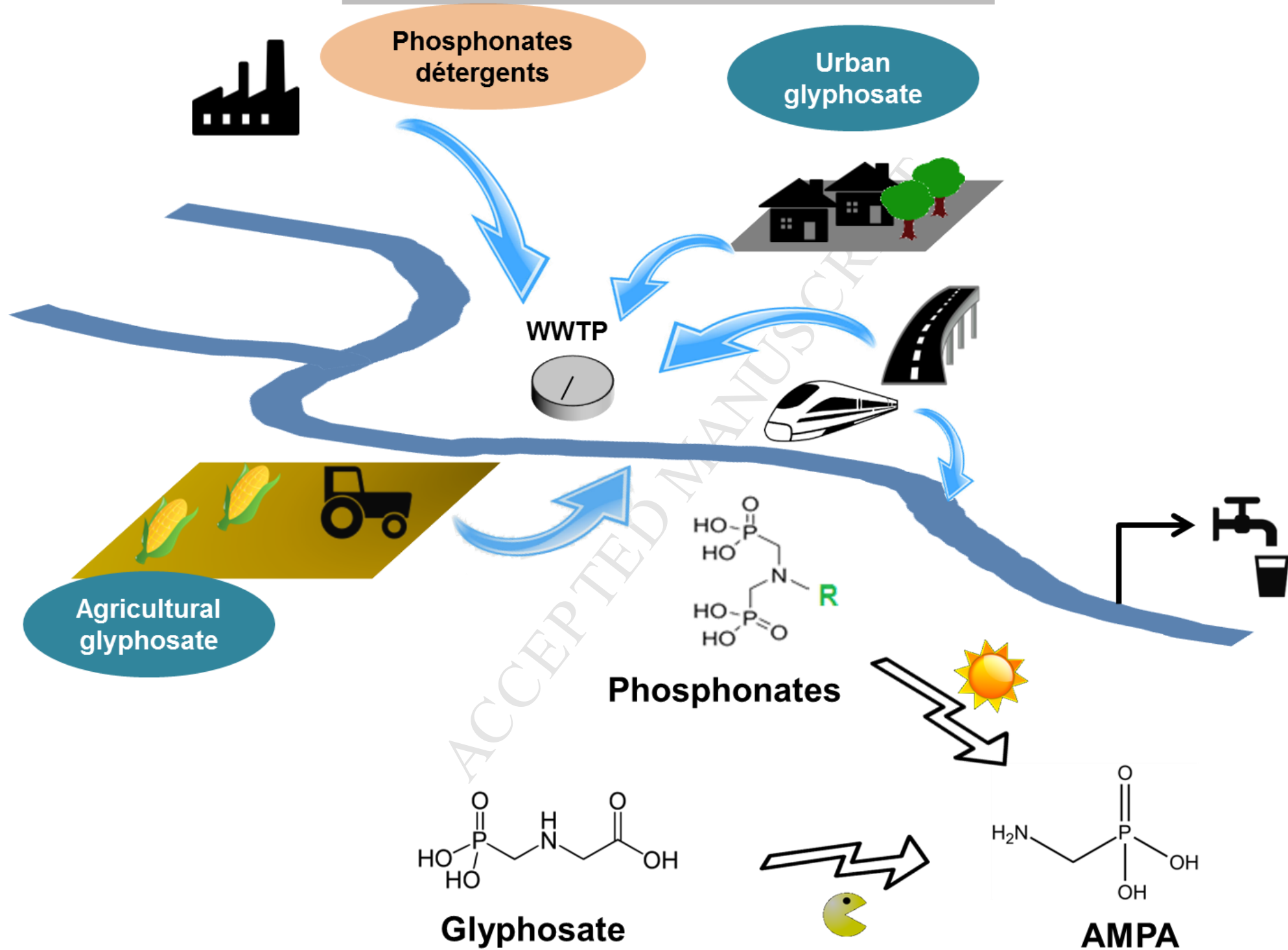
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1 **AminoMethylPhosphonic Acid (AMPA) in natural waters: its**  
2 **sources, behavior and environmental fate**

3 Alexis Grandcoin<sup>1,2,3</sup>, Stéphanie Piel<sup>3</sup> and Estelle Baures<sup>1,2</sup>

4 <sup>1</sup> Environment and Health Research laboratory (LERES), EHESP School of Public Health,  
5 Avenue du Professeur Léon Bernard-CS 74312. Rennes Cedex 35043, France

6 <sup>2</sup> Inserm, U 1085 Institute of Research in Environmental and Occupational Health (IRSET),  
7 Avenue du Professeur Léon Bernard-CS 74312. Rennes Cedex 35043, France

8 <sup>3</sup> SAUR Research and Development, 2 rue de la Bresle, Maurepas 78310, France

9

10 E-Mails: [Alexis.grandcoin@ehesp.fr](mailto:Alexis.grandcoin@ehesp.fr); [Estelle.baures@ehesp.fr](mailto:Estelle.baures@ehesp.fr)

11

12 **Abstract:**

13 The widely occurring degradation product aminomethylphosphonic acid (AMPA) is a result of  
14 glyphosate and amino-polyphosphonate degradation. Massive use of the parent compounds  
15 leads to the ubiquity of AMPA in the environment, and particularly in water.

16 The purpose of this review is to summarize and discuss current insights into AMPA  
17 formation, transport, persistence and toxicity.

18 In agricultural soils, AMPA is concentrated in the topsoil, and degrades slowly in most soils. It  
19 can reach shallow groundwater, but rarely managed to enter deep groundwater. AMPA is  
20 strongly adsorbed to soil particles and moves with the particles towards the stream in rainfall  
21 runoff. In urban areas, AMPA comes from phosphonates and glyphosate in wastewater. It is  
22 commonly found at the outlets of Wastewater Treatment Plants (WWTP). Sediments tend to  
23 accumulate AMPA, where it may be biodegraded. Airborne AMPA is not negligible, but does  
24 wash-out with heavy rainfall. AMPA is reported to be persistent and can be biologically  
25 degraded in soils and sediments. Limited photodegradation in waters exists. AMPA mainly  
26 has its sources in agricultural leachates, and urban wastewater effluents. The domestic  
27 contribution to urban loads is negligible.

28 There is a critical lack of epidemiological data - especially on water exposure - to understand  
29 the toxicological effects, if any, of AMPA on humans. Fortunately, well operated water  
30 treatment plants remove a significant proportion of the AMPA from water, even though there  
31 are not sufficient regulatory limits for metabolites.

32 **Keywords:** *AminoMethylPhosphonic Acid (AMPA); Glyphosate; Metabolite;*

33 **Sources; Watershed**

34

## 35 1. Introduction

36

37 Aminomethylphosphonic acid (AMPA) is a degradation product resulting from phosphonate  
38 degradation (Nowack, 2003; Wang et al., 2016). It can be a metabolite of glyphosate  
39 microbial degradation in soils (Borggaard and Gimsing, 2008), and a photodegradation  
40 product of amino-polyphosphonates in water (Lesueur et al., 2005).

41 AMPA has been reported to occur widely in the air of agricultural areas (Chang et al., 2011;  
42 Battaglin et al., 2014), surface waters (Coupe et al., 2012; Scribner et al., 2007), sediments  
43 (Ronco et al., 2016) and shallow groundwater at depths within 2 m of the edge of the  
44 streams (Van Stempvoort et al., 2014), as well as less frequently in deep groundwater  
45 (Battaglin et al., 2014). Struger et al. (2015) pointed out the uncertainty concerning the  
46 respective proportions of AMPA sources, which can be agricultural, industrial, and urban.

47 Evidence has been found that the sources of AMPA, in a wastewater-influenced stream,  
48 differ depending on hydroclimatic conditions (Botta et al., 2009). Industrial and domestic  
49 phosphonates are an alternative source of AMPA.

50 This paper begins with a review of the current state of knowledge on AMPA sources. Next, it  
51 presents results on AMPA co-transport through the various watershed compartments. This is  
52 followed by a summary of existing data on degradation and persistence, and we conclude  
53 with an update on the known toxicity of AMPA, protection regulations in water, and the state  
54 of the art concerning AMPA in water treatment.

55

## 56 2. Sources of AMPA

57

## 58 2.1. Phosphonates

59

### 60 2.1.1. Origins and spatial dispersion

61

62 Phosphonates are anions of phosphonic acids occurring in environmental pH conditions and  
63 presenting high polarity and high water solubility (Schmidt et al., 2013).

64 Phosphonates (and especially amino-methylene-polyphosphonates) are commonly used in  
65 both industrial and household applications in industrialized countries (Nowack, 2003). Amino  
66 polyphosphonates contain several phosphonic acid groups and at least one amine group.  
67 They are detergents, fire retardants, anticorrosives and anti-scaling agents, and in the textile  
68 industry they are used as complexing agents (Studnik et al., 2015; Nowack, 2003). According  
69 to Studnik et al. (2015) water treatment is the main application of amino-methylene-  
70 phosphonates, which are used as membrane anti-fouling agents.

71 This flexibility of purpose means that they are both useful, and produced. Gledhill and Feijtel  
72 (1992) addressed annual consumption levels of phosphonates in Europe and the USA: the  
73 most popular are nitrilotris-methylenephosphonic acid (NTMP) with 3820 tons in the USA and  
74 3360 tons in Europe; diethylenetriaminepenta-methylenephosphonic acid (DTPMP) with 275  
75 tons in the USA and 5270 tons in Europe; ethylene diamine-tetra-methylenephosphonic acid  
76 (EDTMP) with 0 tons in the USA and 1090 tons in Europe; hexaethylenediamine-tetra-  
77 methylenephosphonic acid (HDTMP) with 180 tons in the USA and 90 tons in Europe; and 1-  
78 Hydroxyethane 1,1-diphosphonic acid (HEDP) with 5270 tons in the USA and 2010 tons in  
79 Europe. Glyphosate (N-phosphono-methylglycine) is also an economically significant  
80 phosphonate, - this subject is tackled at § 2.1.1. Nowack (2004) later reported that worldwide  
81 consumption of phosphonates in 1998 was 56,000 tons, and European consumption was  
82 16,000 tons in 1999. These data may seem outdated, but to the best of our knowledge, these  
83 are the most recent global studies on phosphonate consumption in industrialized countries.

84 Phosphonate chelating agents are used more and more each year in a wide range of  
85 applications (Nowack and Stone, 2002), and some countries, such as France (2007) and the  
86 USA (2010) have banned or limited phosphates in domestic detergents (European  
87 Parliament, 2012), offering yet another application to phosphonates (Studnik et al., 2015).

88 In the UK, phosphonates are currently present in 81% of laundry products and 4% of  
89 dishwasher products, at a rate of 2.5% phosphonates by weight (Comber et al., 2013). Their  
90 fate is not well- documented, mainly for want of a sensitive and specific analytical method.  
91 This lack of adapted analytical method is caused by the ionic and polar nature of  
92 phosphonates (Schmidt et al., 2013).

93 With his previous ion-pair liquid chromatography method development (Nowack 1997b),  
94 Nowack (1997a) spelled out the behavior of major phosphonates in the WWTP, showing that  
95 phosphonates were present in influents at concentrations of between 21-254  $\mu\text{g/L}$  for NTMP,  
96 31-65  $\mu\text{g/L}$  for EDTMP, and 75-974  $\mu\text{g/L}$  for DTPMP. The effluent concentrations were below  
97 detection limits, e.g. 15  $\mu\text{g/L}$  for NTMP, 22  $\mu\text{g/L}$  for EDTMP, and 29  $\mu\text{g/L}$  for DTPMP.  
98 Estimated elimination rates were at least 70%. Phosphonates are concentrated in sludge  
99 rather than degraded (Figure 1); this raises an issue of pollution transport if sludge is used as  
100 fertilizer.

101 Phosphonates can be released into the environment through sewer outfall or WWTP.

102

103

**Figure 1: please insert here**

104

105 2.1.2. Phosphonate degradation pathways

106

107 Biodegradation



108 Because of their strong C-P bond, phosphonates are difficult to degrade. This results in a  
109 prolonged lifetime and accumulation in water environments (Forlani et al., 2011). Phosphates  
110 are preferentially used by microbial fauna as a phosphorus source. Consequently  
111 phosphonates are poorly consumed and degraded under natural conditions (Hsieh and  
112 Wanner, 2010; Nowack, 2003). Several microorganisms have however been identified as  
113 being able to use phosphonates as their only source of phosphorus: *Bacillus megaterium*,  
114 *Pseudomonas aeruginosa*, *Agrobacterium radiobacter*, *Escherichia coli*, *Pseudomonas*  
115 *stutzeri* and *Streptomyces morookaensis* (Obojska and Lejczak, 2003; Kononova and  
116 Nesmeyanova, 2002; Matys et al., 2004).

117 Furthermore, Forlani et al. (2011) successfully used *Spirulina* strains to remove 50% of initial  
118 polyphosphonate pollution from wastewater; although degradation was incomplete, and  
119 potential metabolites are unknown.

120

#### 121 Physical and chemical degradation

122 Thanks to Iron-phosphonate complexes, the main phosphonate degradation pathway under  
123 natural conditions is photodegradation, which enables metal-catalyzed photodegradation  
124 (Nowack, 2003). According to the review by Jaworska et al. (2002), AMPA is the main  
125 degradation product formed by degradation of NTMP, EDTMP, DTPMP. Lesueur et al.  
126 (2005) showed that phosphonates are converted mainly into orthophosphate (93%) and to a  
127 lesser extent into AMPA (7%) under UV light in an aquatic environment. This conversion is  
128 enhanced in the presence of Iron and an acidic pH (Figure 2). AMPA is eventually converted  
129 to orthophosphate.

130

131 **Figure 2: Please insert here**

132

133 The fate and behavior of phosphonates in the environment are poorly described due to the  
134 lack of a sensitive, specific and reliable method for their determination in natural systems  
135 (Lesueur et al., 2005).

136

## 137 2.2. Glyphosate

138

### 139 2.2.1. Origins and spatial dispersion

140

#### 141 Agricultural

142 Glyphosate is the most widely used herbicide in the world, with production of 620,000 tons in  
143 2008 (Bøhn et al., 2014), increasing to 825,000 tons in 2014 (Benbrook, 2016). Introduced in  
144 1974, glyphosate is now extensively used with genetically modified herbicide-tolerant crops;  
145 it is also commonly used for non-agricultural areas (Scribner et al., 2007).

146 Figure 1 shows the fate of glyphosate in a watershed. Applied glyphosate is initially  
147 concentrated in topsoil layers: Yang et al. (2015b) conducted an experiment in an artificial  
148 rain-simulation facility on bare soil. They showed that 72% of the applied herbicide is found  
149 at a depth of between 0 and 2 cm in clay loam soil; Okada et al. (2016) and Rampazzo et al.  
150 (2013) made the same observations for silty clay loam soils and silty loam soils. Glyphosate  
151 sorption in soils is broadly described as strong. Okada et al. (2016) proved that adsorption is  
152 related to soil clay content, CEC (Cation Exchange Capacity), and negatively related to pH  
153 and phosphorus.

154 Conversely, Sidoli et al. (2015), Ololade et al. (2014), and Lupi et al. (2015) found that soil  
155  $\text{pH}_{\text{CaCl}_2}$  and organic carbon (OC) regulate glyphosate behavior in soils. Furthermore,  
156 glyphosate is sorbed onto iron and aluminum oxides (Borggaard and Gimsing, 2008,  
157 Vereecken, 2005, Sidoli et al., 2015, Rampazzo et al., 2013), while sorption onto silicates is

158 limited and soil organic matter (OM), while not itself sorbing glyphosate, does affect  
159 glyphosate sorption by stabilizing oxides with high sorption capacity, according to Borggaard  
160 and Gimsing (2008). For Candela et al. (2010) glyphosate adsorption is mainly a kinetic  
161 process, influenced by pore water velocity and residence time of soil solutions. Surface  
162 complexation and precipitation can happen given slow water speed and lengthy residence  
163 time. If water velocities are slow and enough time is allowed to interact with the soil matrix,  
164 surface complexation and precipitation takes place.

165 Phosphate and glyphosate are chemically similar, and although there could be competition  
166 for sorption sites, phosphates overcome glyphosate on sorption sites in only a few soils and  
167 minerals. Kanissery et al. (2015) have shown that phosphate addition in clay loam soil  
168 decreases glyphosate sorption. However this phenomenon is actually limited or absent for  
169 most soils (Borggaard, 2011).

170 Where strong sorption is demonstrated, glyphosate accumulation in soils can be expected.  
171 La Jeunesse et al. (2015) confirmed that a large amount of glyphosate is stored in a once-  
172 per-year application vineyard catchment and released throughout the year with heavy  
173 rainfall, despite rapid glyphosate degradation in soils, with a half-life of 7-130 days on site.

174

#### 175 Non-agricultural & WWTP

176 Glyphosate use is not confined to agricultural sources. Botta et al. (2009) showed that  
177 contamination of the Orge basin (France) is of urban origin - roads and railways being the  
178 main sources of glyphosate in their study. In addition, Torstensson et al. (2005) have shown  
179 railway maintenance to be a major source of glyphosate contamination in Sweden, because  
180 glyphosate residues were found in railway drainage and nearby groundwater.

181 Lastly, the urban contribution to glyphosate load in surface waters has been studied in recent  
182 years. In France, Blanchoud et al. (2007) reported that urban runoff flows directly towards

183 rivers via separate sewer systems (initially constructed to limit storm water overflow), and this  
184 contributes to the transfer of pollution to surface waters. Connor et al. (2007) showed that  
185 runoff from small-urbanized tributaries may contribute as much or more to the pesticide loads  
186 than runoff from the agricultural areas, in San Francisco Bay. Glyphosate is ubiquitous at  
187 French storm sewer outlets: Zgheib et al. (2012) found glyphosate in water (dissolved plus  
188 particulate phase) with 93% detection frequency.

189 In addition to these general statements, few authors have gained more specific glyphosate  
190 behavior knowledge. A small catchment in Switzerland (25 km<sup>2</sup>), studied by Hanke et al.  
191 (2010) found glyphosate to leach with fast runoff from hard surfaces; glyphosate inputs to  
192 WWTP, sewer system overflow and separate sewer systems account for 60% of glyphosate  
193 load in surface water. Kolpin et al. (2006) studied 10 effluent of WWTP across the USA. They  
194 showed that these WWTP export glyphosate, increasing glyphosate content in the receiving  
195 stream by 100%. Following these initial observations, the origins of glyphosate in urban  
196 effluents called for exploration. Ramwell et al. (2014) and Tang et al. (2015) thus shed light  
197 on the contribution of solely domestic usages to surface water drains, and less than 1% of  
198 applied glyphosate was recovered in drains. They concluded that losses from similar and  
199 European representative residential catchments (5.16 ha with 148 houses, England  
200 (Ramwell et al., 2014) and 9.5 ha with 112 houses, Belgium (Tang et al., 2015)).were  
201 unlikely to contribute significantly to surface water load, in comparison with other urban  
202 areas.

203

204

### 205 2.2.2. Glyphosate degradation pathways

206

207 Biodegradation

208 Glyphosate presents two major degradation pathways (Figure 3), one leading to the  
209 formation of AMPA and the other leading to the formation of sarcosine and glycine  
210 (Borggaard and Gimsing, 2008; Al-Rajab and Schiavon, 2010; Wang et al., 2016). Duke  
211 (2011) showed that glyphosate is already degraded to AMPA in crops and weed. The plant  
212 residues can also export AMPA in soils (Mamy et al., 2016).

213

214 **Figure 3: please insert here**

215

216 Glyphosate sorption in soils facilitates microbial degradation, considered the only  
217 degradation process in soils (Borggaard and Gimsing, 2008). This statement is confirmed by  
218 Kanissery et al. (2015) who did not observe any degradation in sterilized soils, regardless of  
219 oxygenation conditions.

220 Soil redox conditions seems to be significant factors in glyphosate degradation in soils,  
221 according to Kanissery et al. (2015), who established higher microbial degradation rates  
222 under oxic soils than in anoxic soils; 53-63% of the  $^{14}\text{C}$ -glyphosate is mineralized as  $^{14}\text{CO}_2$  in  
223 56 days (oxic), whereas 38-41% of the  $^{14}\text{C}$ -glyphosate is mineralized in 56 days (anoxic).  
224 Unexpectedly, soil phosphate addition stimulates degradation in anoxic soils despite  
225 glyphosate desorption (see 2.2.1) (Kanissery et al., 2015). Glyphosate degradation rates in  
226 soils are not linked to OM and clay content. Degradation rates are positively correlated to soil  
227 pH and to a lesser extent to total metal concentrations (Kools et al., 2005).

228

229 Wang et al. (2016) investigated glyphosate fate in the water-sediment system, showing the  
230 major role played by sediments in degradation. The sarcosine pathway was the first to occur,  
231 associated with microbial growth, whereas the AMPA pathway occurred later under  
232 starvation conditions (lack of nutriment). Both pathways contribute to herbicide degradation

233 in the water-sediment system. Sviridov et al. (2015) listed the strains capable of degrading  
234 glyphosate in different environments, mainly soils and waters. They also specify which  
235 metabolite is mainly created by each microorganism, concluding that among the studied  
236 bacterial strains, AMPA is produced most.

237 Table 1 summarizes the reported half-lives of glyphosate in soils, leading to the formation of  
238 AMPA through biological degradation. Under oxic conditions, glyphosate is degraded quickly  
239 in every soil, and more slowly under anoxic conditions (Kanissery et al., 2015). This confirms  
240 the importance of soil microflora in AMPA formation.

241

242 **Table 1: please insert here**

243

244 Physical and Chemical degradation

245 Chemical degradation and photodegradation are minor glyphosate degradation pathways  
246 under natural conditions (Mallat and Barceló, 1998). Laboratory experiments proved that  
247 glyphosate can be abiotically degraded in water, in the presence of manganese oxides.  
248 0.005 g/L birnessite ( $\delta$ -MnO<sub>2</sub>) typically degrades up to 53% of 0.59 mmol/L of glyphosate in  
249 50 hours (Barrett and McBride, 2005). Later Li et al. (2016) reported that 5 g/L birnessite ( $\delta$ -  
250 MnO<sub>2</sub>) typically degrades up to 70% of 3 mmol/L of glyphosate in 24 hours. Light increases  
251 the degradation rate without affecting the range of degradation. Surface mineral sorption  
252 facilitates the formation of reactive complexes. According to Li et al. (2016) glyphosate  
253 surface sorption is the key factor in influencing the rate and extent of degradation. Sorption of  
254 degradation products onto catalytic surface sites in the mineral decreases both the rate and  
255 extent of the reaction. Ascolani Yael et al. (2014) recently evidenced that AMPA is produced  
256 when glyphosate interacts with metallic ions (Cu<sup>2+</sup>) in an aqueous solution, showing the

257 existence of slight abiotic degradation of glyphosate by metals. Metallic ion concentration  
258 used was 2.7 g/L, e.g. far from natural environment (World Health Organisation, 2004).

259

260 It has been demonstrated that AMPA may be derived from amino-polyphosphonates and  
261 glyphosate. In Europe, which doesn't use GMO crops, there is currently no agreement as to  
262 the contribution of each source to AMPA contamination of natural waters. According to  
263 Struger et al. (2015), occurrences of AMPA in Canadian streams are mainly due to  
264 glyphosate applications in urban and rural areas (agricultural - row crop influenced - or  
265 pristine forest land use) settings. This statement is built on positive correlations between  
266 AMPA and glyphosate occurrences, and a lack of positive correlations between AMPA and  
267 the wastewater tracer acesulfame.

### 268 3. AMPA and glyphosate transport across the watershed

269

270 As a degradation product, AMPA usually co-occurs with glyphosate (Aparicio et al., 2013;  
271 Lupi et al., 2015). In a spatially wide occurrence study, Battaglin et al., (2014) showed that  
272 glyphosate is detected without AMPA in only 2.3% of 3,732 water and sediment samples,  
273 and that AMPA is detected without glyphosate in 17.9% of samples. Therefore, AMPA and  
274 glyphosate have been described together in the literature regarding their transport; in this  
275 paper, we will proceed in the same way.

276

#### 277 3.1. Transport across soil

278

279 Glyphosate and AMPA transport can occur with favorable hydrological factors, where they  
280 are stable in soils, air or water. Van Stempvoort et al. (2016) showed that glyphosate and  
281 AMPA are persistent enough to reach shallow groundwater, be stored in it and then

282 transferred to surface water. Leaching of glyphosate and AMPA through soil seems to be a  
283 slow, minor phenomenon, according to Bergström et al. (2011). This statement is confirmed  
284 by Al-Rajab and Hakami (2014) who showed that less than 1% of the initially applied  
285 glyphosate leached in 2 months in a silty clay loam soil. Moreover Okada et al. (2016) report  
286 that small amounts of glyphosate move quickly, but less than 0.24% of the applied  
287 glyphosate leach beyond a depth of 15cm in agricultural silty clay loam and silty loam soils.  
288 Nevertheless, Napoli et al. (2015) have demonstrated that both glyphosate and AMPA can  
289 leach through 100 cm of silty clay soil. As a percentage of applied glyphosate, 0.2% and  
290 0.58% of glyphosate and AMPA respectively are recovered annually in lysimeters after  
291 leaching through 1 m of silty clay soil.

292 Candela et al. (2010) found glyphosate traces at 1.9 m depth in a weathered granite soil, with  
293 low content in OM and clay, but with Al and Fe oxides and hydroxides. In this granite soil,  
294 AMPA is found to be less mobile than glyphosate. This suggests that, in poor soils with low  
295 content of organic matter and clays in the soils, the herbicide may reach deep soil layers and  
296 then groundwater.

297 Borggaard and Gimsing (2008) stressed the importance of preferential flows combined with  
298 heavy rainfalls shortly after application, for glyphosate and AMPA transport deeper into the  
299 soil profile.

300 Many authors have sought to measure the extent of mobility: Scribner et al. (2007) report  
301 glyphosate and AMPA occurrence in USA groundwater for 5.8% and 9.7% respectively of the  
302 485 sites sampled with maximum concentrations of 0.67 µg/L and 4.7 µg/L. Later, Battaglin  
303 et al. (2014) repeated this type of occurrence study and found glyphosate and AMPA in 5.8%  
304 and 14.3% respectively of 1171 groundwater samples, with a maximum of 2.03 µg/L and  
305 4.88 µg/L.

306 This insight supports the idea that glyphosate and AMPA have low mobility through soils, and  
307 should not represent a major threat for groundwater quality, with a few exceptions due to



308 geological context. AMPA seems to be a slightly more of a threat to groundwater quality than  
309 its parent (Borggaard and Gimsing, 2008; Vereecken, 2005).

310

### 311 3.2. Transport towards surface water

312

313 As previously explained in paragraph 2.2.1., glyphosate is mainly stored in topsoil layers; this  
314 is true also of AMPA. Both can be exported mainly by runoff and by underground leaching  
315 from agricultural soils towards surface water, especially when rainfall occurs shortly after  
316 application (Yang et al., 2015b). Coupe et al. (2012) observed high levels of glyphosate and  
317 AMPA in surface water correlated with fresh application of herbicide. They concluded that  
318 maximal concentration in streams occurs with the first runoff episode after glyphosate  
319 application.

320 According to Yang et al. (2015a), Daouk et al. (2013) and La Jeunesse et al. (2015), rain  
321 intensity is an essential factor for the offsite transport of glyphosate and AMPA; the  
322 generated soil particle movement will carry adsorbed glyphosate and AMPA, which will end  
323 up in surface water where it can be desorbed, degraded, or stored in sediments (Degenhardt  
324 et al., 2012; Todorovic-Rampazzo et al., 2014). Aparicio et al. (2013) conducted a study in  
325 sixteen agricultural sites and forty-four streams in Argentinian agricultural basins, which were  
326 sampled three times during 2012. They showed that AMPA is less influenced by this particle-  
327 affinity and is found in only 20% of suspended particulate matter samples, whereas  
328 glyphosate is found in 67% of samples. Yang et al. (2015b) conducted their experiment in an  
329 artificial rain-simulation facility. They showed that up to 14% of applied glyphosate is  
330 transported in runoff and suspended load from a clay loam soil with a rain intensity of 1  
331 mm/min for 1 hour (extremes conditions of washing). This corroborates with Kjær et al.  
332 (2011) who found that 13-16% of glyphosate leached due to a particle-facilitated transport  
333 from a well-drained loamy field in Denmark (1.26 ha). The study were conducted in a

334 research field where the uppermost meter of the soil is heavily fractured and bioturbated, the  
335 water table is located 1–3 m b.g.s. (Lindhardt et al., 2001). Conversely, Norgaard et al.  
336 (2014) were unable to observe evidence of particle-facilitated transport of glyphosate and  
337 AMPA although they present a leaching risk chart based only on rainfall intensity and  
338 elapsed time after application.

339 With regard to non-agricultural soils, Tang et al. (2015) investigated glyphosate and AMPA  
340 loss mechanisms in a Belgian residential area, with 1 stormwater outlet and during 13  
341 events. The loss mechanisms are mainly governed by rainfall amount and intensity. Less  
342 than 0.5% of initially applied glyphosate is recovered in storm drain outflow after 67 days.  
343 When both glyphosate and AMPA are included in the total load, the loss rate is less than 1%.  
344 These low loss rates can be explained by the residential area's low runoff potential e.g.  
345 runoff from unconnected or indirectly connected hard surfaces which can flow across  
346 pervious surfaces and infiltrate.

347

### 348 3.3. Transport in the atmosphere

349

350 Edge of agricultural field levels of glyphosate and AMPA in air and rain in the USA have been  
351 reported by Chang et al. (2011), who found glyphosate in both air and rain in the range of 60-  
352 100% of collected samples during two crop-growing seasons. AMPA was found in 40-90% of  
353 rain samples and 60-90% of air samples. Wind erosion and spray drift are the main sources  
354 for glyphosate and AMPA transport to the atmosphere. Several consecutive studies  
355 (condensed in Table 2) support these observations, and Battaglin et al. (2014) found  
356 glyphosate and AMPA in more than 70% of 85 rain samples collected at three distant sites.

357 Concentrations of glyphosate and AMPA reached a maximum of 9.1 ng/m<sup>3</sup> and 0.97 ng/m<sup>3</sup>  
358 respectively in air, and 2.5 µg/L and 0.48 µg/L respectively in rain. Weekly rain ≥ 30 mm is  
359 efficient in removing the majority of glyphosate from the air (Chang et al., 2011).

360 Unfortunately, the proportion of applied glyphosate transmitted to the atmosphere is not  
361 known.

362 Despite their low vapor pressure and strong adsorptive trend (Battaglin et al., 2014),  
363 glyphosate and AMPA occur in precipitation, and facilitate contamination transport to  
364 untreated areas.

365

366 **Table2: Please insert here**

367 Transport of AMPA and glyphosate is well documented (Vereecken, 2005), but more realistic  
368 experiments and modelling can be useful for a better understanding of exports by leaching  
369 and runoff. Scarce AMPA airborne data are available. The proportion of applied glyphosate  
370 transmitted to the atmosphere and its fate is unknown (Chang et al., 2011). Long-range  
371 transport of glyphosate and AMPA through the atmosphere has not been studied.

372

#### 373 4. AMPA degradation in the watershed

374

375 AMPA degradation is not well documented because the fate of metabolites has only recently  
376 become a concern. Most sources of information are ambitious studies which were designed  
377 to gain full understanding of glyphosate fate, including that of AMPA in the total glyphosate in  
378 soil and water.

379 AMPA is considered persistent by the Pesticide Properties Database (PPDB, 2015), with a  
380 typical half-life (DT50) of 121 days. According to Bento et al. (2016), AMPA degradation is  
381 mainly a microbial process governed by temperature and soil moisture, in which AMPA  
382 degrades faster with heat and humidity. AMPA DT50 at 30°C ranges between 26 and 45  
383 days in loess soil; DT90 (time after which 90% of the initial AMPA is degraded) ranges

384 between 88 and 148 days. Conversely, Bergström et al. (2011) found correlations between  
385 AMPA degradation rates and amount of OM, observing a half-life of 35 days in clay topsoil  
386 and 98 days in subsoil. Concerning loam top soils, Simonsen et al. (2008) calculated a DT50  
387 of 32 days for AMPA, Zhang et al. (2015) observed AMPA DT50 ranging between 10 and 37  
388 days, and lastly Mamy et al. (2005) observed 25-75 days.

389 AMPA degradation occurs in wetlands, as shown by Imfeld et al. (2013) and Degenhardt et  
390 al. (2012). These authors were not looking for a specific DT50, but did show that AMPA was  
391 more persistent than glyphosate in wetlands.

392 These findings confirm that the rate of AMPA degradation in soils is slower than that of  
393 glyphosate, except for high clay content soils (See Table 1 for Glyphosate degradation)  
394 (Bergström et al., 2011). Aparicio et al. (2013) explained this enhanced persistence by lower  
395 penetrability to cell membranes and stronger adsorption on particles.

396 Li et al. (2016) investigated AMPA degradation kinetics in laboratory experiments, at pH 7,  
397 22 °C, under artificial light with 5 g/L of manganese oxide (birnessite) and 3 mmol/L of  
398 AMPA. Birnessite abiotically oxidizes 70% of initial AMPA in 7 days.

399 Ronco et al. (2016) evidenced that AMPA tends to accumulate in the bottom sediments of  
400 agricultural basin rivers, where it may be degraded by microbial fauna.

401 Presently AMPA is described as persistent and resilient to degradation under natural  
402 conditions (Al-Rajab and Schiavon, 2010; Imfeld et al., 2013). AMPA degradation kinetics in  
403 the environment should be investigated.

404

## 405 5. AMPA public health concerns

406

## 407 5.1. Toxicity

408

409 There is no epidemiological data on AMPA exposure from water. Limited data from in vitro  
410 studies are available, concerning its toxicity to human and animal cells (Cerqueira and Duke,  
411 2010). Within the public health context, we will refer only to human-cell based studies.

412 The metabolite nature of AMPA may lead to questions as to its possible formation in the  
413 body. According to EFSA (2014), it is unlikely that glyphosate degradation to AMPA occurs in  
414 the human body (Niemann et al., 2015). Any AMPA contamination should not, therefore, be  
415 the result of glyphosate exposure. There is a lack of knowledge about AMPA formation from  
416 phosphonates in the body.

417 Kwiatkowska et al. (2014) showed that AMPA induces slight toxic effects on human  
418 erythrocytes (in vitro). From 0.05 mM AMPA induces hemolysis, and from 0.25 mM AMPA is  
419 able to create reactive oxygen species and increase the methemoglobin level in blood.  
420 Regarding human lymphocytes, Mañas et al. (2009) found AMPA to have clastogenic effects  
421 from 1.8 mM. They also noted that from 2.5 mM, Hep-2 DNA suffers significant damage.  
422 Finally, Benachour and Séralini (2009) proved that AMPA causes umbilical membrane cell  
423 damages and occasionally embryonic or neonatal cells death. No occurrence study has been  
424 conducted on blood outside of acute poisoning cases, in which AMPA can reach 2.6 µg/mL  
425 of blood (Han et al., 2016).

426 Surprisingly, Li et al. (2013) showed that AMPA and glyphosate inhibit growth of cancer cells,  
427 but not of healthy cells. The authors propose the development of anticancer therapy based  
428 on AMPA and glyphosate.

429 Mesnage et al. (2012) looked for the occurrence of AMPA in the excretions of a farmer and  
430 his family members and were unable to find AMPA in their urine; the detection limit was 1  
431 µg/L (approximately 9.0 mM), low levels of AMPA in the urine may have been missed.  
432 Hoppe (2013) provided a more accurate method, with a limit of quantification of 0.15 µg/L in

433 urine. 65 urine samples from 182 subjects were AMPA contaminated, with a mean of 0.18  
434  $\mu\text{g/L}$  (approximately 1.6 mM). However, the author does not specify the type of population  
435 studied. Exposure and assimilation routes may differ depending on occupation, residence  
436 area, and diet. To establish comparisons, future studies should pay attention to the possible  
437 exposures of populations. Niemann et al. (2015) reviewed the occurrence of glyphosate in  
438 the urine of Europeans and Americans, concluding that AMPA and glyphosate are poorly  
439 correlated and suggesting that AMPA has other sources than glyphosate biodegradation.  
440 Hoppe (2013) analyzed 182 adults urine samples from 18 European countries. The ratios  
441 AMPA/Glyphosate are very variable in the sampled urines. It suggests that European  
442 populations, exposure to amino-polyphosphonates is added to glyphosate exposure

443

## 444 5.2. Policy framework: water

445

446 In Europe, anthropogenic compounds and potential other pollutants are now monitored in  
447 water, in line with the 98/83/CE European Council directive (1998). Raw waters cannot be  
448 used to produce drinking water where any individual pesticide (including metabolites)  
449 exceeds 2  $\mu\text{g/L}$ , or if total pesticides (including metabolites) exceed 5  $\mu\text{g/L}$  (JORF, 2007).  
450 This policy also limits each compound to 0.1  $\mu\text{g/L}$  in drinking water, and 0.5  $\mu\text{g/L}$  for total  
451 pesticides (including metabolites). Designed to control pesticides, the directive has been  
452 frequently updated and extended to cover monitoring of pertinent degradation products and  
453 pharmaceuticals.

454 Elsewhere, to the best of our knowledge, regulatory policies concerning pesticides are less  
455 stringent in India, Australia, Canada, and USA. These countries have individually established  
456 pesticide thresholds, but do not regulate metabolites (Bhushan et al., 2013; NHMRC, 2016;  
457 Health Canada, 2014; US EPA, 2016). For example, the maximum admissible level of  
458 glyphosate in drinking water in the USA is 700  $\mu\text{g/L}$ . It is 1000  $\mu\text{g/L}$  in Australia, 280  $\mu\text{g/L}$  in

459 Canada and absent from Indian policy (Bureau of Indian Standards, 2012). The World Health  
460 Organization (WHO) in 2011, did not suggest formal guidelines for AMPA and glyphosate  
461 (WHO, 2011), but the WHO reviewed its position in 2015 and declared glyphosate “probably  
462 carcinogenic to humans” (Guyton et al., 2015) . Moreover, Guyton et al. (2015) mentioned  
463 that AMPA can induce oxidative stress which leads to chronic inflammation and from there  
464 other unfavorable outcomes. Recently, the European Chemicals Agency gave an opposite  
465 opinion and did not declared glyphosate as carcinogenic to humans, neither mentioned  
466 AMPA (European Chemicals Agency, 2017).

467 Phosphonates are not mentioned by the WHO, probably because of the lack of studies  
468 concerning their behavior, toxicity and degradation.

469

### 470 5.3. Drinking water treatment

471

472 AMPA occurrence has frequently been reported in the various resources. AMPA is found in  
473 groundwater at levels ranging from few thousandths  $\mu\text{g/L}$  to several tenths  $\mu\text{g/L}$  (Van  
474 Stempvoort et al., 2014; Scribner et al., 2007; Van Stempvoort et al., 2016; (Battaglin et al.,  
475 2014). Van Stempvoort et al. (2016) found AMPA in shallow groundwater at depths within 2  
476 m of the edge of the streams, with a detection frequency of 5% of analyzed samples. Earlier,  
477 Scribner et al., (2007) reported results for two different groundwater surveillance programs.  
478 AMPA detection frequency in the first program was 9.7% of 485 samples, with a maximum of  
479  $0.62 \mu\text{g/L}$ . In the second program concerning an agricultural watershed, AMPA detection  
480 frequency was 72.6% of 117 samples, with a maximum of  $2.6 \mu\text{g/L}$ .”.

481 In a French agricultural watershed, Piel et al. (2012) showed that AMPA occurs widely in  
482 streams all year round. Moreover, maximum AMPA concentrations appear to be higher in  
483 urban ( $5 \mu\text{g/L}$ ) than rural areas ( $2 \mu\text{g/L}$ ). In their broad study, Battaglin et al. (2014) showed  
484 that in USA streams, mean AMPA concentration is  $0.2 \mu\text{g/L}$ , and can reach  $28 \mu\text{g/L}$  with a

485 detection frequency of 71.6% of analyzed samples. In large rivers, mean AMPA  
486 concentration is 0.22 µg/L and can reach 4.4 µg/L, with a detection frequency of 89.3% of the  
487 analyzed samples. Many other worldwide studies on water confirm these trends (Poiger et  
488 al., 2016; Scribner et al., 2007).

489 Given that AMPA frequently occurs in water resources, the water treatment plants need to be  
490 able to remove AMPA.

491 AMPA removal is rarely documented; few authors report that AMPA removal or degradation  
492 can be achieved through common treatments. Sand filtration and bank filtration are  
493 moderately effective in AMPA elimination (25-95%), accommodating degrading microbiome  
494 and sorption sites for the pollutant (Jönsson et al., 2013). According to Hall and Camm  
495 (2007), coagulation/clarification of AMPA efficiency is uneven, ranging from 10% to 80%,  
496 depending on pH, coagulant type and dose.

497 As has been shown previously, AMPA is glyphosate's main biodegradation and  
498 photodegradation product in the environment, and this is also true for chemical oxidation  
499 (Brosillon et al., 2006; Mehrsheikh et al., 2006). Simple UV disinfection does not remove  
500 AMPA from drinking water (Brosillon et al. 2006; Assalin et al. 2010; Klinger et al. 1998).  
501 Chlorination using a HOCl/herbicide molar ratio greater than 2 provides full degradation of  
502  $10^{-4}$  M of glyphosate at pH 7 for 24 hours in the dark (Brosillon et al., 2006). These  
503 conditions were used to represent the water residence time in the distribution network.

504 Batch laboratory tests showed that Ozonation of 42.28 mg/L glyphosate with 14 mg/L  $O_3$  at  
505 pH 10 for 30 minutes removes almost 100% of the residues, including AMPA. Nevertheless,  
506 with pH adjustment at 6.5, degradation is incomplete and produces AMPA (Assalin et al.,  
507 2010). Advanced processes such as  $H_2O_2$ /UVC are effective in fully degrading 50 mg/L of  
508 glyphosate and then AMPA, providing basic pH (7-10), 80 W irradiation, and 2.2 to 5.9 mM of  
509  $H_2O_2$  for 5 hours (Manassero et al., 2010). AMPA is poorly eliminated by granular and  
510 powdered activated carbon – moreover, because activated carbon tends to remove residual



511 O<sub>3</sub> and chlorinated oxidants, it can decrease AMPA oxidation (Besnault et al. 2015; Jönsson  
512 et al. 2013). Besnault et al. (2015) showed that a granular activated carbon (GAC) treatment  
513 process has good initial efficiency in terms of AMPA removal (>90%). However, from 2.5 m<sup>3</sup>  
514 of treated water per kg of GAC, the pilot performance falls to 30-70% of elimination, and less  
515 than 30% beyond 16 m<sup>3</sup>/kg GAC.

516 These statements reveal how sensitive the processes are; they need to be optimized  
517 according to pollutant load and context. In many countries drinking water regulations do not  
518 include metabolites. Moreover the toxicological and epidemiological knowledges are  
519 insufficient or inappropriate to set a guideline (Benachour and Séralini, 2009).

520

## 521 **Conclusions**

522

523 Our review has shown that AMPA can have multiple sources; the main one seeming to be  
524 glyphosate degradation in agricultural soils. This is explained by the short DT50 of  
525 glyphosate and the higher resilience to degradation of amino-polyphosphonates. Moreover,  
526 the vast diversity of uses of the herbicide leads to wide contamination, allowing AMPA  
527 formation in many sections of the environment.

528 AMPA presents a low risk of leaching through soils. It occurs in groundwater having specific  
529 hydroclimatic and geomorphic conditions. Shallow groundwater is at greater risk of AMPA  
530 contamination, particularly where it is close to agricultural surfaces. Surface water bodies are  
531 vulnerable to contamination by AMPA. Rainfall intensity and the amount of time since  
532 application govern the export of AMPA towards surface waters. High adsorptive qualities  
533 induce AMPA-particle bonding, providing transport. Airborne AMPA is significant in  
534 agricultural areas.

535 AMPA is reported to be persistent; it tends to accumulate in soils if not leached. AMPA is  
536 substantially biodegraded only in OM-rich soils. In water, AMPA presents limited physical  
537 and chemical degradation, related to manganese oxides. It accumulates in sediments, where  
538 microbial degradation can occur.

539 In vitro studies have shown evidence of AMPA toxicity to human cells at low concentrations.  
540 A manifest lack of water-exposure epidemiological data prevents any conclusion being drawn  
541 about AMPA safety in water. Current, tolerant water policies across the world demonstrate  
542 the uncertainties around AMPA. Its sources are poorly identified by responsible water  
543 professionals, and seasonal related flows remain unknown. Fortunately, various water  
544 treatment processes can be effective in removing AMPA through adequate adjustments and  
545 temporal targeting. This does however raise concerns about rural catchments inherently  
546 exposed to contamination, and often without water treatment.

547

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549

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552

553 **References**

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**Table 1: Biological degradation of glyphosate in soils, leading to AMPA (Batch laboratory)**

Soil	Glyphosate half-life (DT50) (days)			
	Topsoil (0-30 cm)		Subsoil (30-80 cm)	
	Oxic	Anoxic	Oxic	
Silty clay loam	18	45		Kanissery et al. (2015)
	14.5			Al-Rajab et Hakami (2014)
	19			Al-Rajab et Schiavon (2010)
Silt loam	15	51		Kanissery et al. (2015)
	18	42		
Sand	16.9		36.5	Bergström et al. (2011)
Clay	110		151	
Loam	9			Simonsen et al. (2008)
Loess	3.5			Yang et al. (2015b)
	1.5 - 53.5			Bento et al. (2016)
Clay Loam	7.1			Mamy et al. (2016)
	10.6			Druart et al. (2011)
	4			Al-Rajab et Schiavon (2010)
Sandy loam	14.5			Al-Rajab et Schiavon (2010)

Table 2: Glyphosate and AMPA concentrations in rain

	Location	Samples	% detection	[Glyphosate] ( $\mu\text{g/L}$ )		% detection	[AMPA] ( $\mu\text{g/L}$ )	
				max	median		max	median
Scribner et al. (2007)	USA	14	86.0	1.1	0.274	86.0	0.47	0.113
Battaglin et al. (2014)		85	70.6	2.5	0.11	71.8	0.48	0.04
Chang et al. (2011)	Mississippi 2007	11	73.0	1.9	0.2	73.0	0.3	0.1
	2008	19	68.0	1.6	0.15	74.0	0.48	< 0.1
	Iowa 2007	14	71.0	2.5	0.2	36.0	0.2	< 0.1
	2008	24	63.0	1.8	0.1	50.0	0.24	< 0.1
	Indiana 2004	12	92.0	1.1	0.14	92.0	0.47	< 0.1
Van Stempvoort et al. (2016)	Canada	15	86.7	0.135	-	26.7	0.019	-

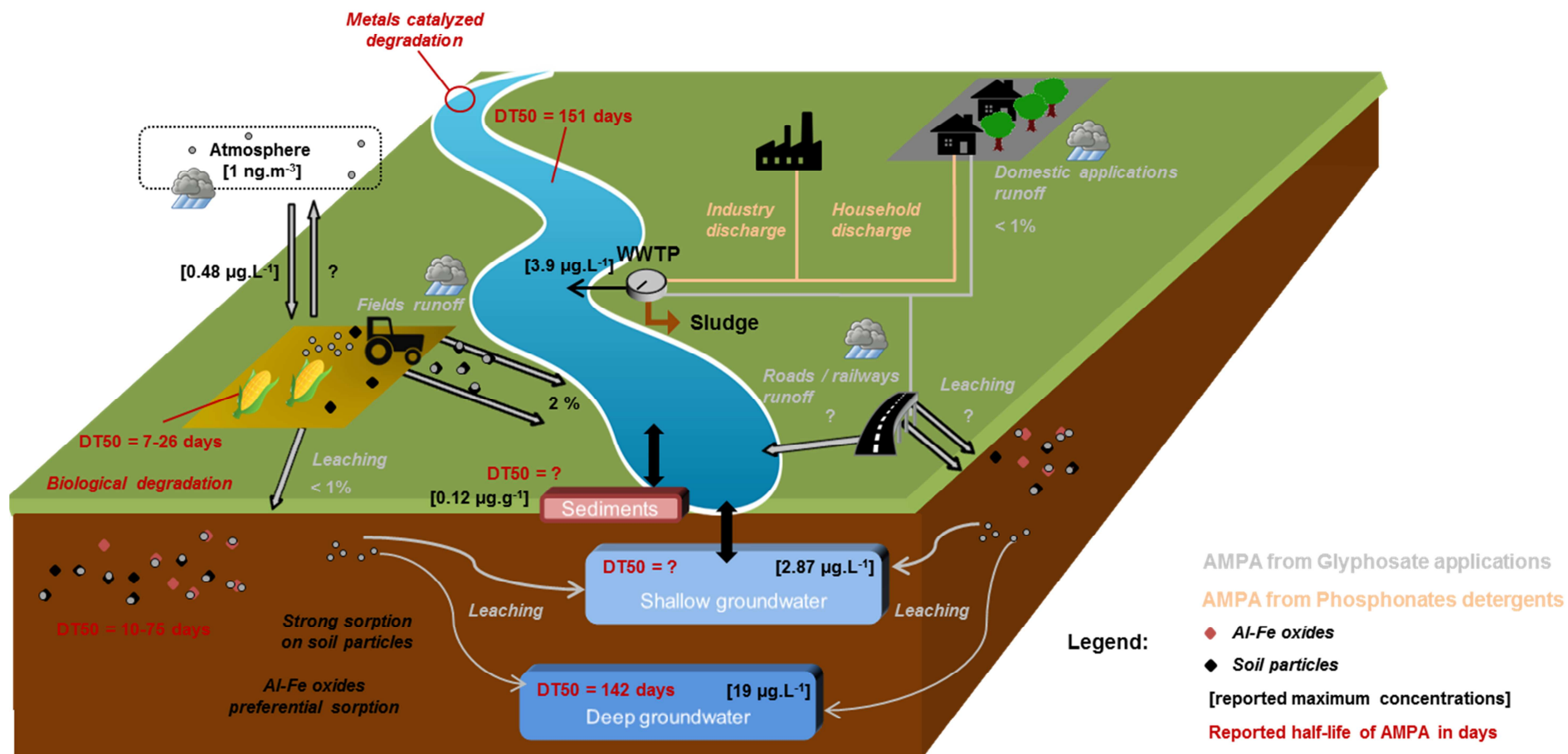


Figure 1: AMPA in natural waters: its sources (glyphosate and phosphonates), behavior and environmental fate

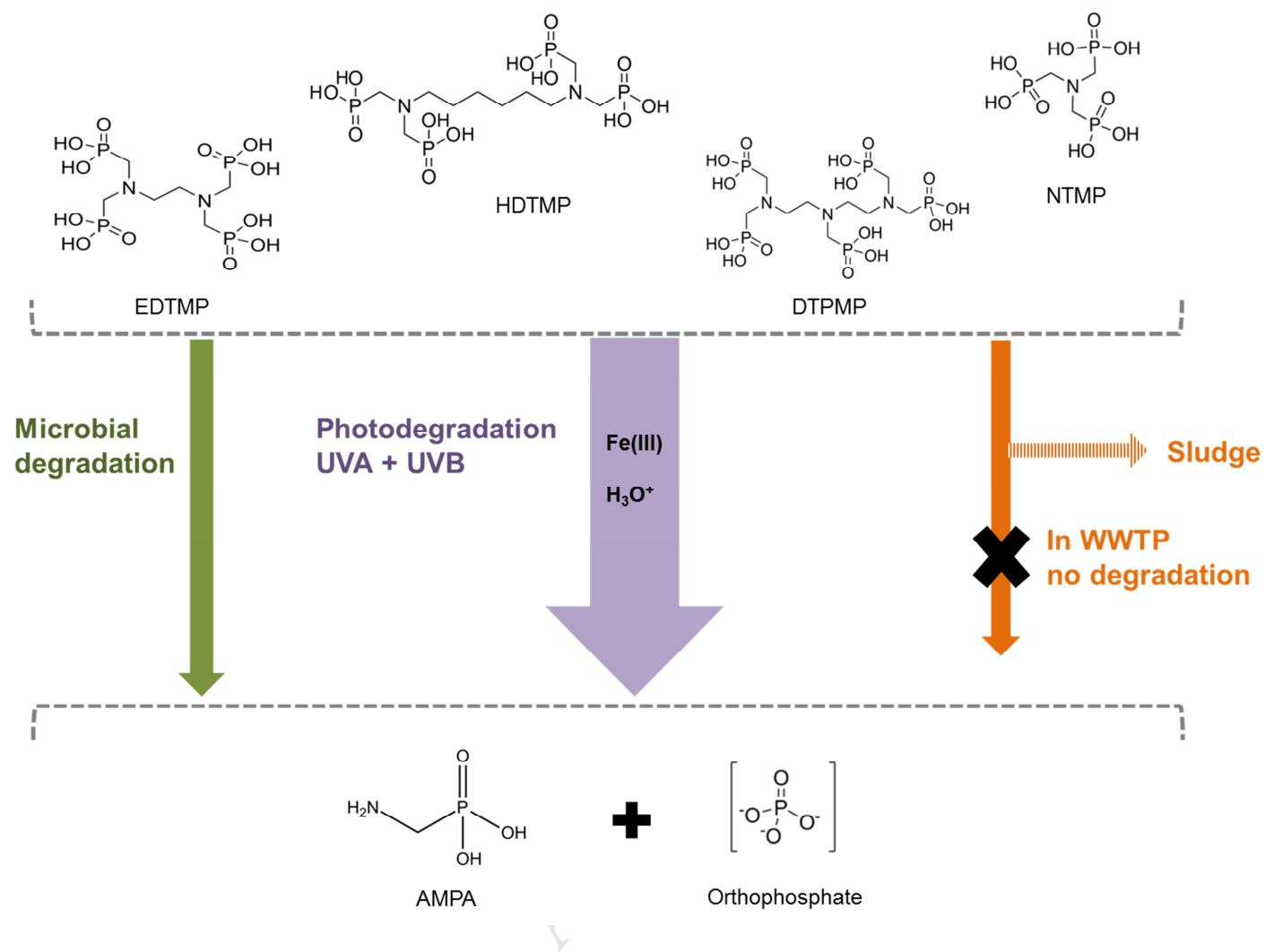
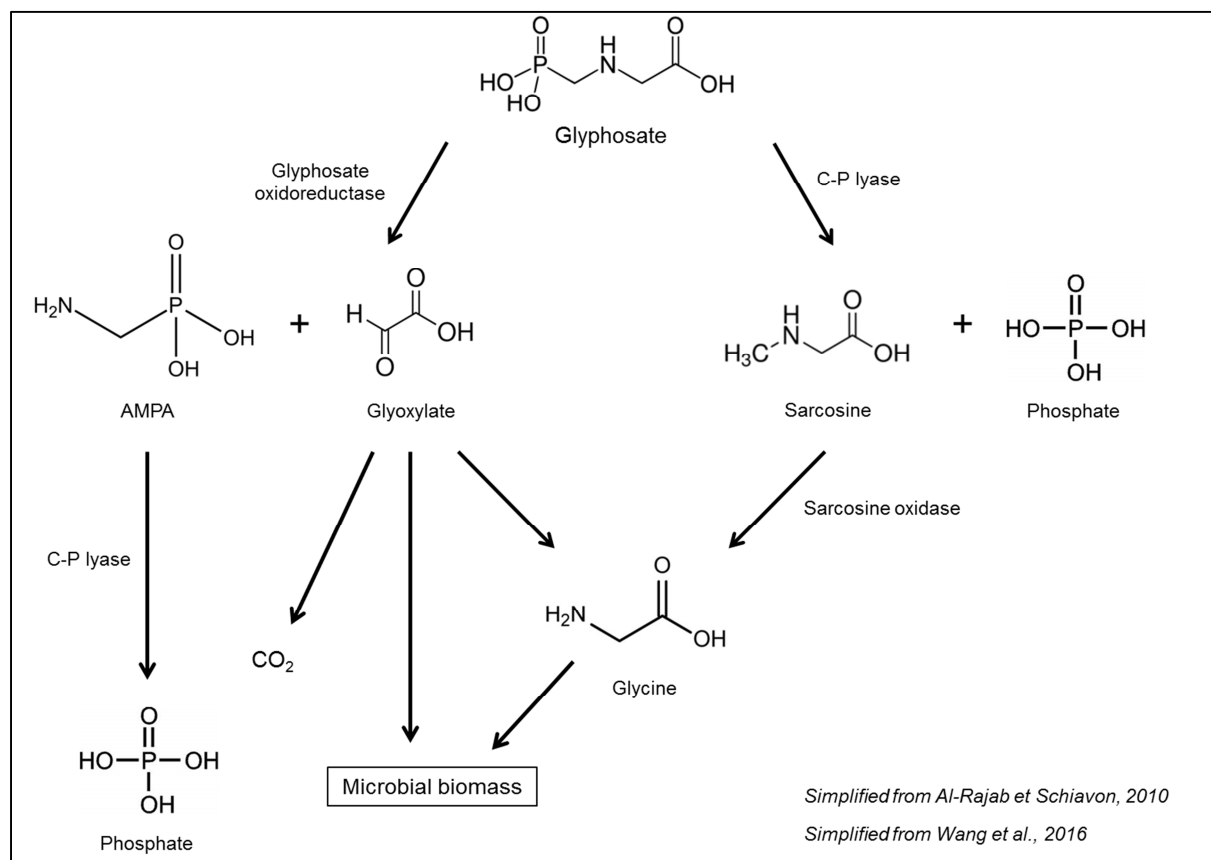


Figure 2: Phosphonate degradation pathways to AMPA in the aquatic environment





**Figure 3: Main glyphosate biodegradation pathways in the environment**

- AMPA is ubiquitous in all environmental compartments, particularly water.
- AMPA is derived from urban phosphonates, and glyphosate.
- Off-site movement of AMPA is mainly due to rainfall, towards surface waters.
- AMPA is persistent but can be biologically degraded in soils and sediments.
- Harmful effects of AMPA are currently unknown due to a lack of studies.