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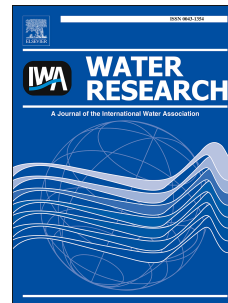
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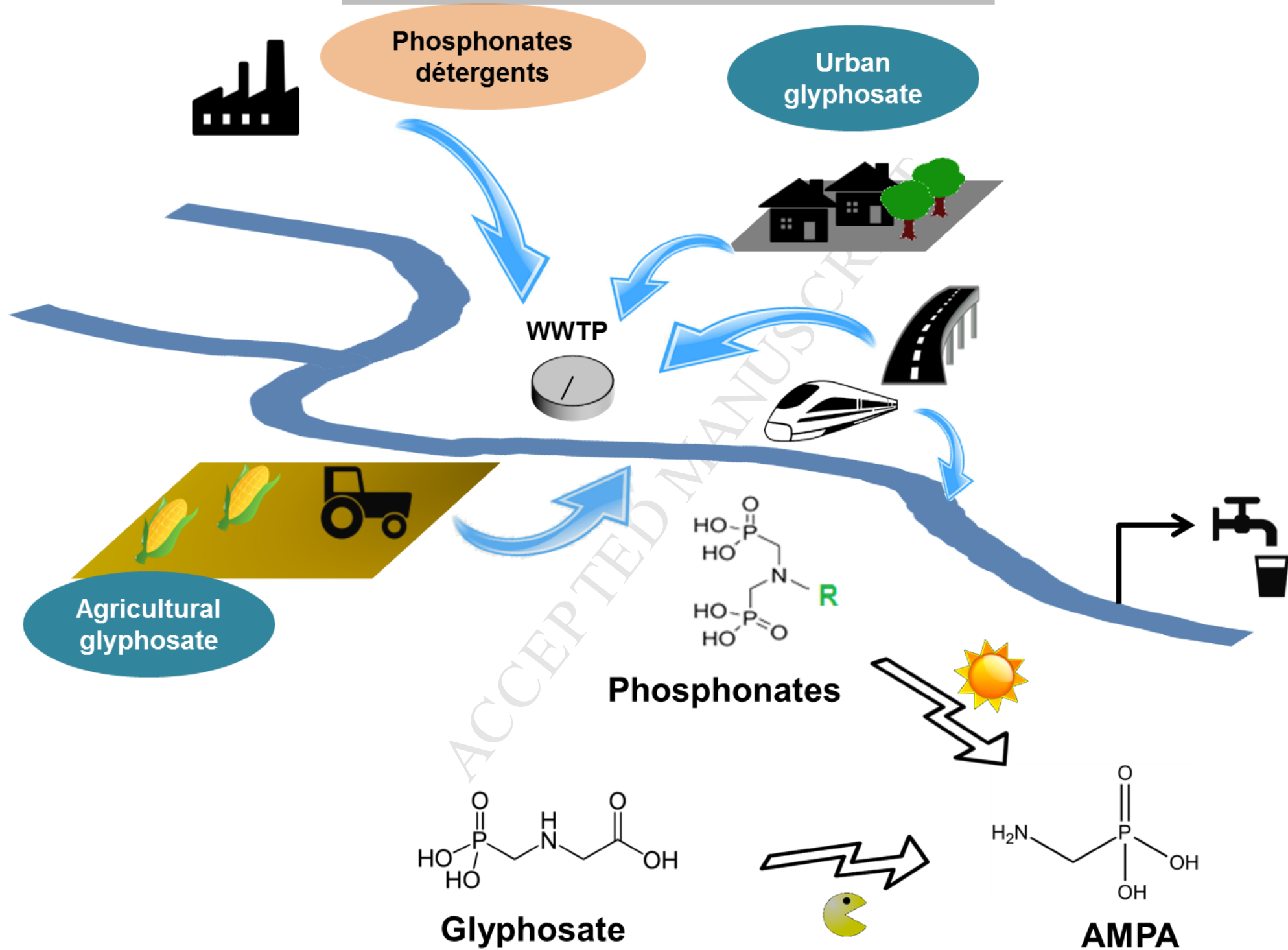
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1 **AminoMethylPhosphonic Acid (AMPA) in natural waters: its**
2 **sources, behavior and environmental fate**

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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 km²), 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}C -glyphosate is mineralized as $^{14}\text{CO}_2$ in
223 56 days (oxic), whereas 38-41% of the ^{14}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 (δ - MnO_2) 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 (δ -
250 MnO_2) 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^{2+}) 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^3 and 0.97 ng/m^3
358 respectively in air, and $2.5 \text{ }\mu\text{g/L}$ and $0.48 \text{ }\mu\text{g/L}$ respectively in rain. Weekly rain $\geq 30 \text{ mm}$ 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 (Cerdeira 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 O₃ 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 H₂O₂/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 H₂O₂ 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 O₃ 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 m³
514 of treated water per kg of GAC, the pilot performance falls to 30-70% of elimination, and less
515 than 30% beyond 16 m³/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	-

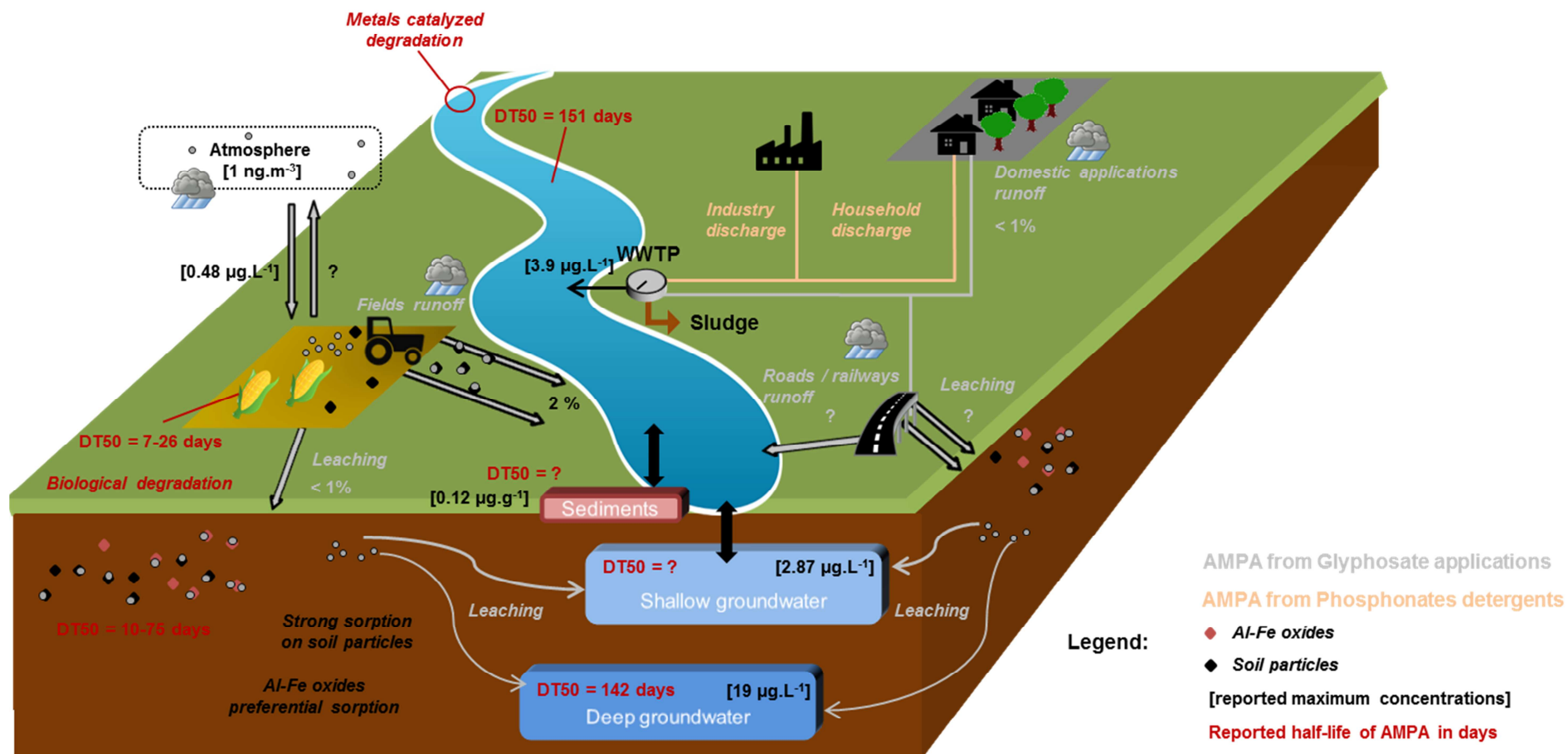


Figure 1: AMPA in natural waters: its sources (glyphosate and phosphonates), behavior and environmental fate

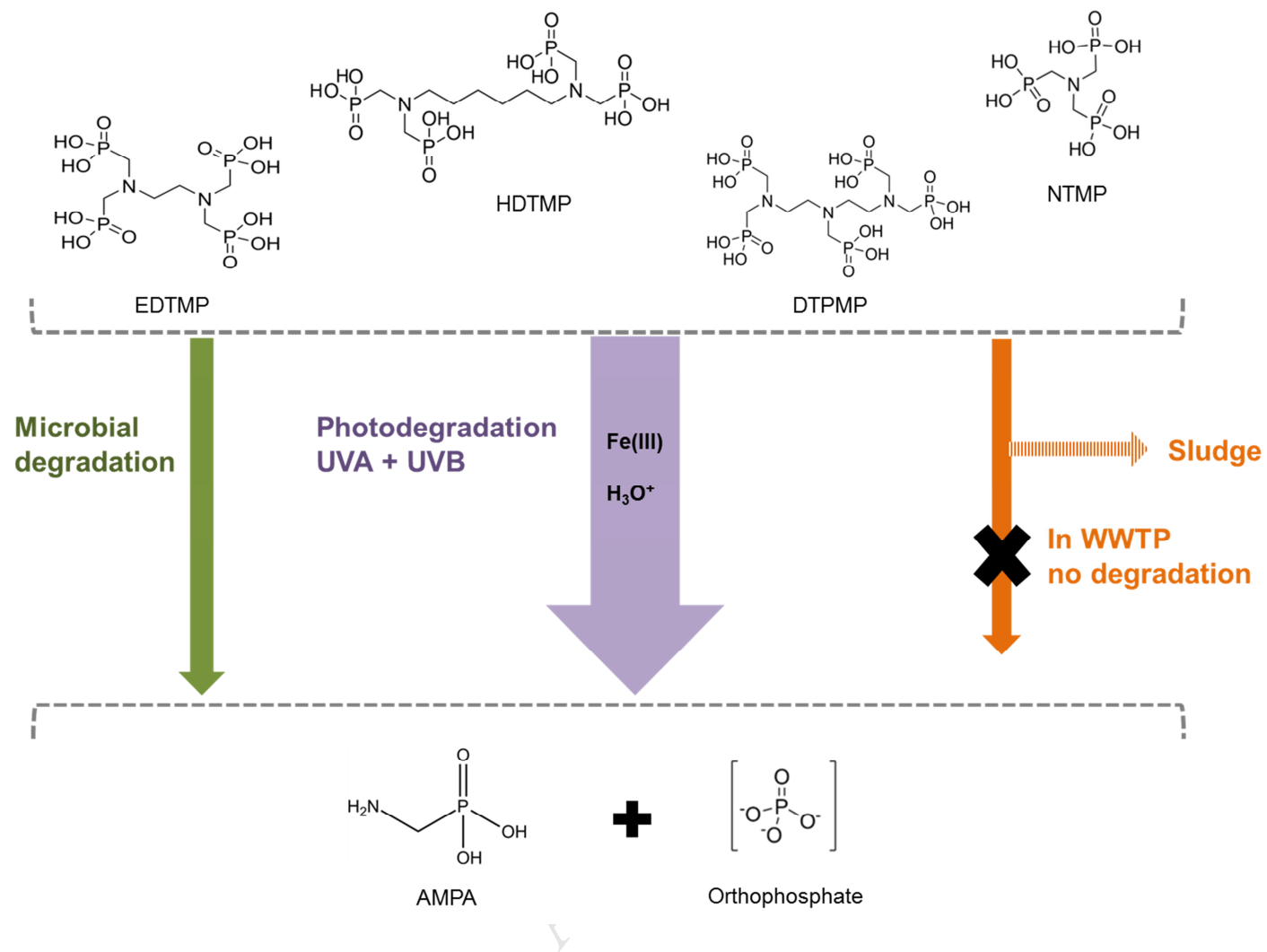


Figure 2: Phosphonate degradation pathways to AMPA in the aquatic environment

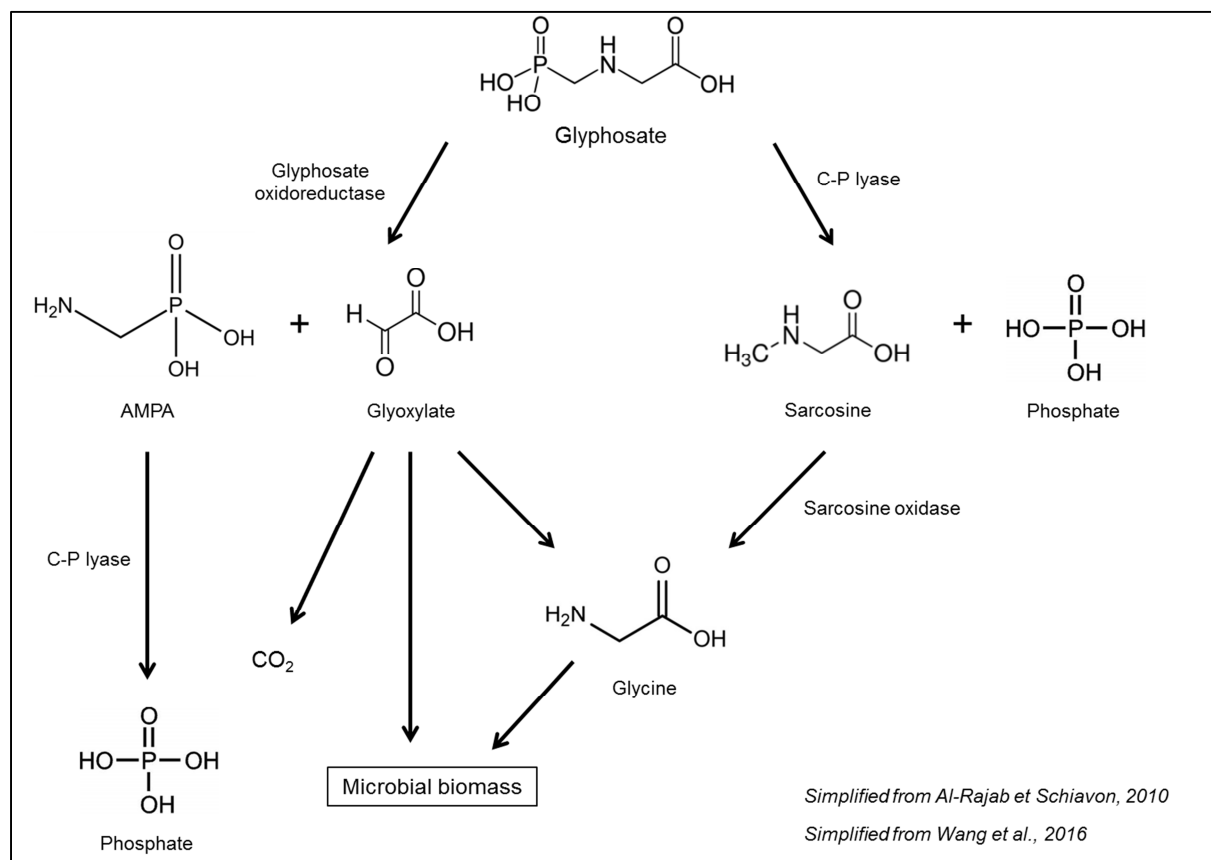


Figure 3: Main glyphosate biodegradation pathways in the environment

- 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.