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

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Abstract:

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

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

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

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

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

Sources; Watershed

1. Introduction

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

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

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

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

2. Sources of AMPA

2.1. Phosphonates

2.1.1. Origins and spatial dispersion

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

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

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

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

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

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

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

Figure 1: please insert here

2.1.2. Phosphonate degradation pathways

Biodegradation

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

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

Physical and chemical degradation

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

Figure 2: Please insert here

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

2.2. Glyphosate

2.2.1. Origins and spatial dispersion

Agricultural

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

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

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

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

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

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

Non-agricultural & WWTP

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

Lastly, the urban contribution to glyphosate load in surface waters has been studied in recent 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.

205 2.2.2. Glyphosate degradation pathways

207 Biodegradation

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

Figure 3: please insert here

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

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

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

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

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

Table 1: please insert here

Physical and Chemical degradation

Chemical degradation and photodegradation are minor glyphosate degradation pathways under natural conditions (Mallat and Barceló, 1998). Laboratory experiments proved that glyphosate can be abiotically degraded in water, in the presence of manganese oxides. 0.005 g/L birnessite (δ -MnO₂) typically degrades up to 53% of 0.59 mmol/L of glyphosate in 50 hours (Barrett and McBride, 2005). Later Li et al. (2016) reported that 5 g/L birnessite (δ -MnO₂) typically degrades up to 70% of 3 mmol/L of glyphosate in 24 hours. Light increases the degradation rate without affecting the range of degradation. Surface mineral sorption facilitates the formation of reactive complexes. According to Li et al. (2016) glyphosate surface sorption is the key factor in influencing the rate and extent of degradation. Sorption of degradation products onto catalytic surface sites in the mineral decreases both the rate and extent of the reaction. Ascolani Yael et al. (2014) recently evidenced that AMPA is produced when glyphosate interacts with metallic ions (Cu²⁺) in an aqueous solution, showing the

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

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

3. AMPA and glyphosate transport across the watershed

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

3.1. Transport across soil

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

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

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

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

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

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

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

3.2. Transport towards surface water

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

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

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

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

3.3. Transport in the atmosphere

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

Concentrations of glyphosate and AMPA reached a maximum of 9.1 ng/m³ and 0.97 ng/m³ respectively in air, and 2.5 µg/L and 0.48 µg/L respectively in rain. Weekly rain ≥ 30 mm is efficient in removing the majority of glyphosate from the air (Chang et al., 2011).

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

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

Table2: Please insert here

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

4. AMPA degradation in the watershed

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

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

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

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

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

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

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

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

5. AMPA public health concerns

5.1. Toxicity

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

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

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

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

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

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

5.2. Policy framework: water

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

Elsewhere, to the best of our knowledge, regulatory policies concerning pesticides are less stringent in India, Australia, Canada, and USA. These countries have individually established pesticide thresholds, but do not regulate metabolites (Bhushan et al., 2013; NHMRC, 2016; Health Canada, 2014; US EPA, 2016). For example, the maximum admissible level of 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

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

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

5.3. Drinking water treatment

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

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

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

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

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

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

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

O₃ and chlorinated oxidants, it can decrease AMPA oxidation (Besnault et al. 2015; Jönsson et al. 2013). Besnault et al. (2015) showed that a granular activated carbon (GAC) treatment process has good initial efficiency in terms of AMPA removal (>90%). However, from 2.5 m³ of treated water per kg of GAC, the pilot performance falls to 30-70% of elimination, and less than 30% beyond 16 m³/kg GAC.

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

Conclusions

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

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

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

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

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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] (µg/L)		% detection	[AMPA] (µg/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.