Review of studies analysing glyphosate and aminomethylphosphonic acid (AMPA) occurrence in groundwater

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1 Review of studies analysing glyphosate and aminomethylphosphonic acid (AMPA) occurrence in
2 groundwater

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Draft

Abstract

The herbicide glyphosate (N-phosphonomethylglycine) has been the most commonly applied herbicide worldwide for the past 40 years. This review aims to present and discuss the state of knowledge concerning groundwater contamination by glyphosate and its metabolite, aminomethylphosphonic acid (AMPA). A dataset of 48 reports and articles reporting glyphosate and AMPA detection in groundwater worldwide was constructed from published literature. Specific attention was given to the analysis of available studies on glyphosate and AMPA transport in groundwater to investigate groundwater contamination factors. The information presented in this review highlights detectable groundwater contamination in several countries globally, with many cases exceeding European groundwater quality standards. Both agricultural and non-agricultural applications of glyphosate can be significant sources of pollution, and proximity to agricultural fields is a significant risk factor. AMPA has two primary sources, glyphosate and amino polyphosphates, but very little information is available about the origin of AMPA detected in groundwater. Glyphosate and AMPA transport to groundwater can be significant in well-structured soils rich in macropores, where it generally occurs via preferential flow. An inverse relationship was highlighted between the groundwater depth and glyphosate and AMPA occurrence and concentration in groundwater; however, some discrepancies among the studies were identified. Heavy rainfall shortly after glyphosate application poses a high risk of its transport to groundwater. Seasonal trends in glyphosate and AMPA in groundwater, related to application timing, agronomic practices, and weather conditions, were also observed. Finally, risk-management measures are proposed.

29

30 Keywords: glyphosate; AMPA; groundwater; leaching; transport.

31 1. Introduction

32 Glyphosate (N-phosphonomethylglycine; $C_3H_8NO_5P$) is a non-selective, systemic, broad-spectrum, and post-
33 emergent herbicide. It is the most commonly used herbicide worldwide, with an estimated use of 825,000 kg
34 in 2014 (Statista 2018). The applications of glyphosate include weed control on transgenic glyphosate-
35 resistant crops, pre-harvest desiccation of cereals, and total weed control both in agricultural fields and in
36 non-agricultural settings, such as urban areas or along roadways and railways. In terms of chemical
37 characteristics, glyphosate is a small molecule with three polar functional groups (carboxyl, amino, and
38 phosphonate groups), and behaves as an amphoteric molecule (Borggaard and Gimsing 2008). It is highly
39 polar and soluble in water (10.5 g/L at 20 °C) (Table 1), and gets strongly adsorbed onto variable-charge
40 surface sites in the soil, particularly iron and aluminium oxides (Gimsing et al. 2004a; Sidoli et al. 2016).
41 Glyphosate is moderately persistent, with a DT50 value (time for the dissipation of 50% of the initial
42 concentration) in the soil, which ranges from 9.4 to 700 days (Lewis et al. 2016).

43 Glyphosate in the environment is primarily degraded by microorganisms, which use it as a carbon and
44 phosphorus source. The degradation rate is higher under aerobic conditions than under anaerobic conditions
45 (Duke 2020). The enzymatic reactions involved in microbial degradation lead to the cleavage of either the
46 C–N or C–P bond, resulting in aminomethylphosphonic acid (AMPA) or sarcosine, respectively, as
47 metabolic products. AMPA is the main metabolite of glyphosate and is an aminophosphonate with a primary
48 amine group. AMPA is polar and highly soluble in water (1467 g/L at 20 °C) and is more persistent in the
49 environment than glyphosate (DT50 = 283.6 – 633.1 days). Owing to these characteristics, it tends to
50 accumulate in the soil (Simonsen et al. 2008; Lewis et al. 2016) (Table 1). Similar to glyphosate, the
51 adsorption of AMPA is related to amorphous aluminium and iron oxides. According to Báez et al. (2015)
52 and Sidoli et al. (2016), AMPA has the same high adsorption range as glyphosate, and they seem to be
53 sorbed to the same extent without any apparent competition for adsorption sites. Nevertheless, it seems that
54 glyphosate and AMPA might not sorb the same way onto the soil, despite their similar atomic compositions.
55 Sidoli et al. (2016) observed that the availability of adsorption sites limits AMPA adsorption to a greater
56 extent than glyphosate, as demonstrated by the low values of the $1/n_f$ coefficient for AMPA, indicating
57 saturation of the adsorption sites with increasing equilibrium concentrations. The difference in the ionic state
58 of glyphosate and AMPA may also affect their relative tendencies for sorption and their mobility in the

subsurface, including groundwater. AMPA occurs in the dissociated state in the soil (Traas and Smit 2003), having pKa values of 1.8 (pKa₁), 5.4 (pKa₂), and 10.0 (pKa₃) (Chen et al. 2009), whereas glyphosate is a zwitterion with four ionic equilibrium constants, pKa₁ = 0.8 [1st phosphonic], pKa₂ = 2.23 [carboxylate], pKa₃ = 5.46 [2nd phosphonic], and pKa₄ = 10.14 [amine] (Tomlin CDS 1997). Variations in pH that modify glyphosate and AMPA's ionic state and the sorption sites on the surface of amorphous oxides can strongly affect their adsorption and mobility (Sidoli et al. 2016). This effect was observed in the case of competition with phosphate at the adsorption sites. Both glyphosate and AMPA compete with available phosphate for the same adsorption sites on oxide surfaces (Sprankle et al. 1975; de Jonge et al. 2001; Gimsing and Borggaard 2002; Gimsing et al. 2004a, 2007), but higher competitive adsorption was observed between phosphate and AMPA than glyphosate in soils with pH_{CaCl2} ranging from 5.4 to 7.0 (Sidoli et al., 2016). One possible explanation lies in the very similar adsorption mechanisms of phosphate and AMPA, which, between pH 5.4, and 7.0, have the same ionic form (1⁻) unlike glyphosate, which has an additional negative charge (2⁻). Indeed, in the above-mentioned pH range, glyphosate has the carboxylic acid group deprotonated and both glyphosate and AMPA have the amino group positively charged and the phosphonic acid group predominantly doubly ionized.

The vulnerability of groundwater to contamination by pesticides via soil is determined by a combination of factors, including the characteristics of the pesticides themselves (e.g. adsorption, degradation, and solubility) and site-related factors such as climate, land use, and soil and hydrogeological conditions (Worrall et al. 2002; Arias-Estévez et al. 2008). Given the strong tendency to adsorb to soil components, glyphosate and AMPA have been commonly considered to have a low groundwater leaching potential (Borggaard and Gimsing 2008). However, several studies have also shown that soil adsorption and degradation of glyphosate and AMPA vary greatly variation depending on soil properties (Gimsing et al. 2004a, 2004b; Yu and Zhou 2005; Mamy et al. 2008; Borggaard and Gimsing 2008; Simonsen et al. 2008; Zablotowicz et al. 2009; Okada et al. 2016, 2019; Sidoli et al. 2016; Bento et al. 2016) , and numerous studies have reported the potential of glyphosate and AMPA for vertical transport to groundwater suggesting that the soil is not always an effective defence against contamination. Moreover, some studies have shown that glyphosate and AMPA can move downward through the soil via preferential flow under certain conditions through macropores and cracks, leading to a significant risk of reaching groundwater (Vereecken

2005; Kjær et al. 2011). Previous work has shown that AMPA is more persistent and slightly more mobile than glyphosate in the soil (Kjær et al. 2005; Kolpin et al. 2006; Mamy et al. 2008; Annett et al. 2014; Okada et al. 2018; Erban et al. 2018), thus increasing the likelihood of its presence in groundwater.

Groundwater contamination by glyphosate can occur via several different pathways, classified as either point or nonpoint sources (Figure 1) (Annett et al. 2014). The point sources correspond to specific release points, such as hard surfaces or locations where chemical handling and application equipment or tanks are cleaned or stored (such as the farmyard) (Carter 2000). Point sources of glyphosate can also be from applications on roads, railways, and urban sealed surfaces, such as parking lots. Point sources are relatively easy to identify, and mitigation is often possible by introducing best management practices for pesticide handling and use.

Non-point sources, which result from agricultural applications in the field, represent the largest proportion of glyphosate contamination and are more difficult to identify and mitigate (Reichenberger et al. 2007). Examples of diffuse glyphosate inputs into groundwater are leaching through the soil and unsaturated zone and infiltration through riverbanks and riverbeds. Pesticide metabolites are sometimes more ubiquitous and abundant than their parent molecules, and this has also been reported for AMPA (Kolpin et al. 2004; Van Stempvoort et al. 2014). This is partly because glyphosate is not the only precursor of AMPA in the environment; AMPA can also originate from amino polyphosphonates degradation. These compounds are commonly used in household and industrial applications, including water treatment materials (Figure 1) as well as detergents, fire retardants, anticorrosives, antiscaling agents, and complexing agents in the textile industry (Nowack 1998; Jaworska et al. 2002; Struger et al. 2015; Wang et al. 2016; Grandcoin et al. 2017). The extensive use of both glyphosate and amino polyphosphonate leads to the ubiquity of AMPA in the environment, particularly in water, and makes it difficult to quantify the relative importance of different sources of AMPA in the environment (Grandcoin et al. 2017).

Groundwater contamination by glyphosate and AMPA is a subject of great importance because groundwater provides almost half of all drinking water worldwide (Smith et al. 2016). High pesticide concentrations in groundwater could be a risk factor affecting drinking water production because simple groundwater treatment steps (sand filtration and aeration) and subsequent steps such as chlorination, ozonisation, and irradiation do not always effectively remove these pollutants. To protect human health, worldwide regulatory jurisdictions have established pesticide drinking water maximum concentration levels (Table 2). The

115 Directive 2006/118/EC of the European Union established a groundwater quality standard for an individual
116 pesticide or degradation product of 0.1 µg/L, and a combined limit value for more than one plant protection
117 product and their degradation products of 0.5 µg/L (European Union 2006). Less conservative limits or
118 guidelines for glyphosate in drinking water have been established in Mexico (10 µg/L) (SEGOB. Productos y
119 servicios 2015), Canada (280 µg/L) (Health Canada 2019), Argentina (300 µg/L) (Argentinean National
120 Guidelines for Human Consumption ANGHC, 2003), Brazil (500 µg/L) (Brasil. Ministry of Health 2016),
121 the United States (700 µg/L) (U.S. Environmental Protection Agency 2009), and China (700 µg/L) (Ministry
122 of Health, PRC 2006).

123 Given the large-scale and intensive use of glyphosate and the uncertainties that still concern the potential of
124 glyphosate and AMPA for transport to groundwater under different conditions, the general objective of this
125 review is to provide an overview of the available scientific literature on the contamination of groundwater by
126 glyphosate and AMPA. The specific aims of this study were to (a) determine the relationship between the
127 detected contamination and aquifer characteristics; (b) evaluate how different pollution sources (agricultural
128 and non-agricultural) contribute to the contamination; (c) to identify whether seasonal trends in the
129 occurrence and concentration of glyphosate and AMPA are evident; (d) determine the relationship between
130 glyphosate and AMPA occurrence in groundwater, and (e) compare the contamination in groundwater with
131 that of other environmental waters.

132

133 2. Approach

134 The present review considers the literature that specifically investigated the occurrence and concentration of
135 glyphosate and/or AMPA in groundwater. A search for studies on glyphosate and AMPA contamination of
136 groundwater was carried out in which peer-reviewed articles, conference proceedings, and grey literature
137 (e.g. theses, government papers, organisation reports, consultant reports, and data from national
138 environmental monitoring programs) were collected. Publications were obtained through Scopus, Google
139 Scholar, Web of Science, and Science Direct scientific literature search engines using combinations of the
140 following keywords: 'glyphosate', 'aminomethylphosphonic acid', 'AMPA', 'groundwater', 'drinking
141 water', 'aquifer', and 'leaching'. English search terms were used to conduct all searches. No date, language,
142 or document-type restrictions were applied during the searches. The search was then expanded using

143 citations in relevant papers and the existing literature. After removing duplicates, the references were
144 screened for relevance at the title and abstract levels. Studies in which the monitored substance was not the
145 active ingredient glyphosate and/or the metabolite AMPA were excluded. Literature surveys presenting the
146 results of other studies were included at this stage only if the original articles, reports, or datasets could not
147 be retrieved. Abstracts referring to a conference contribution that did not contain data or for which
148 information was not available were not considered. Relevant references at the title and abstract levels were
149 assessed for relevance at the full-text level. Studies that investigated the occurrence and concentration of
150 glyphosate and/or AMPA in groundwater are considered relevant. Studies in which glyphosate was applied
151 in a mixture with other pesticides were considered relevant. Articles that did not provide detailed study
152 information or results were excluded. Articles presenting model-based predictions of groundwater pollution
153 by glyphosate and AMPA without information on the measured occurrences of compounds in groundwater
154 were excluded. Furthermore, studies that used groundwater samples pre-selected for being free from
155 glyphosate and AMPA to validate analytical methods for glyphosate and AMPA determination, without
156 providing information about the concentrations in the tested groundwater samples and without applying the
157 method to real water samples, were rejected in the selection process. Inclusion/exclusion criteria are shown
158 in Figure 2.

159 Following the criteria presented above, 48 reports and articles reporting glyphosate and AMPA detection in
160 groundwater worldwide were collected. For each article, the following features were identified if available
161 (Table 3): (i) location; (ii) site description; (iii) number of samples; (iv) depth of groundwater sampled (m
162 below ground surface); (v) time of collection; (vi) glyphosate detection limit ($\mu\text{g/L}$); (vii) AMPA detection
163 limit ($\mu\text{g/L}$); (viii) percentage of glyphosate detection in samples, (ix) percentage of AMPA detection in
164 samples, (x) maximum glyphosate concentration observed ($\mu\text{g/L}$), (xi) maximum AMPA concentration
165 observed ($\mu\text{g/L}$), (xii) median glyphosate concentration observed ($\mu\text{g/L}$), and (xiii) median AMPA
166 concentration observed ($\mu\text{g/L}$).

167 The information reported in the collected articles varies widely in terms of scope and experimental setup,
168 number of samples, detection limits, concentrations reported, and considerations regarding the occurrence or
169 non-occurrence of glyphosate and AMPA. Therefore, no attempt has been made to use statistical methods to

170 combine data from multiple studies; instead, the state of knowledge about groundwater contamination by
171 glyphosate and AMPA was qualitatively analysed and discussed.

172

173 3. Findings

174 3.1 Overview of studies

175 The articles in Table 3 are grouped by geographical areas (Europe, North America, South America, Asia, and
176 Oceania) and then by country. The studies span a period of 25 years, from 1996 (when the earliest analysed
177 paper was published) to 2021. More than 50% of the articles were published after 2016, revealing increasing
178 concern regarding groundwater pollution by glyphosate and its metabolite AMPA. Of the 48 articles, 33
179 analysed glyphosate and AMPA, whereas the other 15 considered glyphosates but not AMPA. Table 3 shows
180 that most studies were conducted in Europe (21 studies in 13 European countries) and the Americas (21
181 studies comprising five countries); three studies were carried out in Asia (China and Sri Lanka) and three in
182 Oceania (New Zealand and American Samoa). Regarding the type of investigation, seven studies were field
183 trials designed to determine the groundwater contamination resulting from the application of glyphosate-
184 based products (Smith et al. 1996; Grunewald et al. 2001; Ramwell et al. 2004; Kjær et al. 2005; Candela et
185 al. 2010; Crowe et al. 2011; Jing et al. 2021), whereas the other 41 were environmental monitoring aimed at
186 investigating the contamination of groundwater at different spatial scales (from local/municipal to national).
187 Glyphosate was detected in groundwater at concentrations above the limit of detection (LOD) in 37 out of 48
188 studies, whereas among the 33 studies analysing AMPA, 22 found AMPA above the LOD. It should be
189 noted that there is large variability in LODs between the studies reported in Table 3, especially regarding
190 glyphosate. The reported LOD for glyphosate ranged from 0.0005 µg/L (Hanke et al. 2008) to 100 µg/L (de
191 Oliveira et al. 2020), whereas for AMPA, the LOD ranged from 0.0001 µg/L (Hanke et al. 2008) to 1.03
192 µg/L (Correia et al. 2020).

193 The occurrence and detected concentrations of glyphosate and AMPA varied widely among different
194 countries and study sites. Among all considered studies, the maximum reported concentration ranges from
195 0.021 µg/L (Pazikowska-Sapota et al. 2020) to 45 µg/L (Smith et al. 1996) for glyphosate and 0.020 µg/L
196 (Haarstad and Ludvigsen 2007) to 19 (Horth and Blackmore 2009) µg/L for AMPA. In European countries,
197 where growing genetically modified crops are not allowed, the maximum reported concentration was 24

198 $\mu\text{g/L}$ for glyphosate and $19 \mu\text{g/L}$ for AMPA, both detected in France in 2005 (Horth and Blackmore 2009).
199 Compared with the concentrations detected in Europe, the studies conducted in the American continent
200 reported a higher maximum concentration of glyphosate, namely $45 \mu\text{g/L}$ for glyphosate detected by Smith
201 et al. (1996) in Canada, and a lower maximum concentration of AMPA, being $6.5 \mu\text{g/L}$ for AMPA, detected
202 by Demonte et al. (2018) in Argentina. In Europe (Horth and Blackmore 2009; Abrantes et al. 2010; Sanchís
203 et al. 2012; Mörtl et al. 2013; Székács et al. 2015; ISPRA 2018; Pazikowska-Sapota et al. 2020; SLU Centre
204 for Pesticides in the Environment (CKB) 2020), there have been observations above the groundwater quality
205 standard of $0.1 \mu\text{g/L}$ for drinking water (European Union 2006), whereas no detections in the other countries
206 were above the relevant standards or guidelines considered. In Mexico, one groundwater well presented a
207 concentration higher than the maximum limit allowed for drinking water ($10 \mu\text{g/L}$; SEGOB. Productos y
208 Servicios, 2015); however, according to the authors, the exclusive irrigation use of this groundwater should
209 not cause concern. It is essential to note that the European drinking water standard is much more
210 conservative than the guidelines established by Mexico, Canada, Argentina, Brazil, the United States,
211 and China. Considering the European drinking water standard, several other studies conducted outside the
212 European Union (Smith et al. 1996; Scribner et al. 2007; Haarstad and Ludvigsen 2007; Crowe et al. 2011;
213 Battaglin et al. 2014; Ruiz-Toledo et al. 2014; Van Stempvoort et al. 2014, 2016; Olivo et al. 2015; Poiger et
214 al. 2017; Rendón-Von Osten and Dzul-Caamal 2017; Hadfield 2017; Demonte et al. 2018; Gunarathna et al.
215 2018; Okada et al. 2018; Montoya et al. 2019; Welch et al. 2019; Reynoso et al. 2020; Correia et al. 2020;
216 Lutri et al. 2020; Mas et al. 2020; Pires et al. 2020; Close et al. 2021; Geng et al. 2021) found concentrations
217 above the threshold.

218

219 3.2 Relationship between unsaturated and saturated zonal characteristics and groundwater contamination

220 Glyphosate and AMPA can be persistent enough to reach the groundwater, especially in the presence of
221 favourable hydrological factors (in terms of soil depth, infiltration capacity, texture, structure, and
222 groundwater depth). Leaching of glyphosate and AMPA has been well documented; according to Borggaard
223 and Gimsing (2008) and de Jonge et al. (2000), it appears to be favoured in structured soils with preferential
224 flow pathways through macropores. However, although leaching indicates an increased risk of groundwater
225 pollution, the occurrence of glyphosate and AMPA in leachate does not automatically mean that they will

reach groundwater. Numerous other factors determine groundwater contamination risk, including geologic conditions, aquifer characteristics (water table depth, transmissivity, water circulation, redox conditions), and agronomic practices (tillage systems, mitigation measures, rotation, etc.). These factors, their relationships, and the complex dynamics that rule groundwater contamination by glyphosate and AMPA have been investigated in several field trials and environmental monitoring studies. These two main categories of studies will be discussed separately because each offers insight from different points of view and at different levels of complexity.

233

3.2.1 Field trials

Field trials in which groundwater contamination was evaluated following the application of glyphosate are essential for understanding the complex mechanisms that govern glyphosate and AMPA transport. Candela et al. (2010) conducted a field experiment to monitor glyphosate and AMPA leaching through weathered granite soils located in Spain (Maresme region) under irrigated and non-irrigated conditions. The application rate was 8.6 kg/ha, which is at least three times higher than doses generally applied in European countries (0.4–2.5 kg/ha a.i.), although the authors claimed that it aligns with the standard agricultural practice in the Maresme area. Glyphosate and AMPA were never detected in shallow groundwater during the monitoring period (87 and 92 days after the irrigated and non-irrigated plot treatments, respectively). Nevertheless, glyphosate and AMPA leached through the soil much more in-depth than expected according to the calculated distribution coefficients, probably due to preferential transport and colloid-mediated transport, highlighting the potential risk of glyphosate and AMPA transport to groundwater. They suggested that in soils with low organic matter and clay content, these molecules may reach deep soil layers and groundwater, especially in the case of abundant recharge generated by irrigation and heavy rain, and possible preferential flow and colloidal mediated transport.

Glyphosate transportation to a deeper soil layer can also occur because of root exudation. When applied to weeds, glyphosate is absorbed by the plant leaves and rapidly translocated to developing apical and root meristems (Grangeot et al. 2006). Glyphosate can return to the soil by root exudation (Coupland and Caseley 1979) by passing the first 30–50 cm of soil, where degradation should be favoured compared to deeper layers. The amount of herbicides that return to the soil with plants can be significant (Laitinen et al. 2007;

254 Doublet et al. 2009). The higher persistence and accumulation of glyphosate in the lower layer of the soil can
255 increase the potential risk of glyphosate and AMPA transport to groundwater.

256 In Denmark, Kjær et al. (2005) conducted an extensive study within the framework of the Danish Pesticide
257 Leaching Assessment Program, aiming to examine glyphosate transport and leaching risk under field
258 conditions. In this study, tile-drainage water, groundwater, and soil water were sampled over two years from
259 three sites treated with glyphosate: one sandy site and two loamy sites. Their results suggested that
260 glyphosate and AMPA leaching through the soil could be significant under specific conditions. At one of the
261 loamy sites, glyphosate and AMPA leaching into the tile drain occurred, with average concentrations
262 exceeding 0.1 µg/L. The detection frequency in tile-drainage water was 100% for both compounds in the
263 first year, whereas in the second year, glyphosate and AMPA were detected in 52% and 93% of the samples,
264 respectively. The transport of these compounds was mainly determined by storm events, suggesting that
265 leaching could be primarily ascribed to the preferential flow through macropores in the soil, which, as
266 revealed by field observations, was well structured and rich in macropores and sand-filled fissures. However,
267 despite the evidence of glyphosate and AMPA leaching in tile-drainage water, the detection of these
268 compounds in groundwater was sporadic, accounting for only three samples containing glyphosate, in
269 concentrations ranging from 0.01 to 0.04 µg/L. The authors pointed out that beneath the drainage system, the
270 decreased hydraulic conductivity facilitates the dispersion, dilution, adsorption, and degradation of these
271 molecules, limiting further transport to groundwater. In contrast, leaching was absent in the sandy site and
272 minor in the other loamy site. The strong adsorption capacity and the lack of macropores prevented
273 glyphosate and AMPA leaching at the sandy site, whereas the low rainfall amount and intensity at the loamy
274 site allowed the substances to adsorb and degrade, thus minimising leaching.

275 Intrinsic soil characteristics as well as tillage practices could affect the amount of glyphosate and AMPA
276 transported through the soil profile. Tillage practices affect pore size distribution and connectivity, which in
277 turn affect flow and solute transport (Lipiec et al. 2006). In particular, conservation tillage systems, such as
278 no-tillage, minimise soil disturbance and leave the soil surface layer's structure mostly intact, yielding a
279 higher amount of continuous macropores, which can favour the preferential flow of water and solutes. In
280 contrast, conventional tillage, which includes ploughing, disking, and harrowing, largely disrupts the
281 preferential paths, resulting in uniform flow and transport in the upper disturbed layer (Jarvis et al. 2007).

282 This could lead to the inference that no-tillage increases pesticide leaching compared to conventional tillage.
283 However, contrasting results have been obtained from different studies (Fomsgaard et al. 2003; Gjettermann
284 et al. 2009; Larsbo et al. 2009; Rampazzo et al. 2013; Okada et al. 2014, 2016), suggesting that the effect of
285 soil tillage on pesticide leaching might depend more on the initial soil conditions and climatic conditions
286 than on tillage practices (Alletto et al. 2010). Given the discrepancies between the existing studies, it is
287 difficult to clearly identify the influence of conservation agriculture alone on glyphosate and AMPA
288 transport through soils to groundwater.

289 The presence of soil horizons that restrict water flow can affect the transport of glyphosate to groundwater.
290 Smith et al. (1996) examined glyphosate levels in well water from three sub-stations in Newfoundland,
291 Canada. the first sub-station was located on a well-drained site, whereas the soil of the second and third sub-
292 stations was characterised by constricting layers (fragipans). The sub-stations were sprayed with a 2%
293 solution of Roundup to control weeds (application rate of 4.3–4.6 kg/ha a.i), and well water sampling was
294 carried out for 32 weeks following treatment. In the second and third sub-stations, glyphosate concentration
295 was below the limits of detection throughout the study, whereas in the first sub-station, glyphosate was
296 detected in all samples of well water with concentrations ranging from 7.2 to 45 µg/L. The second and third
297 substations soils had a fragipan layer, characterised by a loamy subsurface horizon with high bulk density
298 and low hydraulic conductivity. This layer could have restricted the vertical infiltration of water and
299 glyphosate migration to the water table, preventing groundwater contamination.

300 Grunewald et al. (2001) reported the importance of climatic conditions, particularly the rainfall regime, in
301 the period after treatment. They monitored glyphosate and AMPA concentrations in soil and water (shallow
302 groundwater, runoff, and reservoir water) for six months after applying a glyphosate-based herbicide (May–
303 August 1998) in a catchment located in Saxony, Germany. They observed that glyphosate and AMPA were
304 not found above the LOD in any groundwater samples, and they completely dissipated from the soil five
305 months after the treatment. The authors concluded that glyphosate and AMPA's high affinity for soil and dry
306 weather during the test period should have significantly limited their mobilisation rate through the soil.

307

308 3.2.2 Monitoring studies

309 Various monitoring studies provide information on the occurrence of glyphosate and AMPA in groundwater.

Pinto et al. (2018) in Portugal, Hanke et al. (2008) in Switzerland, Kolpin et al. (2004) in the United States, and Primost et al. (2017) in Argentina monitored glyphosate and AMPA in groundwater at different spatial scales (from local to national), but they did not find these molecules above the LOD in any samples. Among the studies that monitored glyphosate but not AMPA, no detection of glyphosate was reported by Ramwell et al. (2004) in the United Kingdom, de Oliveira et al. (2020) and Santos et al. (2020) in Brazil, and Jing et al. (2021) in China. Primost et al. (2017), who monitored soil, surface water, and groundwater in a central agricultural district in Mesopotamic Pampas, Argentina, found that despite glyphosate and AMPA not being detected in groundwater, they were ubiquitous in soil samples with very high maximum concentrations (about 8 and 39 mg/kg for glyphosate and AMPA, respectively) and were also detected in 27%–55% of the surface water samples with concentrations of up to 1.8 and 1.9 µg/L for glyphosate and AMPA, respectively. The authors postulated that the lack of detection in groundwater was likely due to interacting factors, such as the high adsorption tendency of glyphosate and AMPA, especially in the investigated soils, and the depth of the aquifer (40–60 m). The same consideration was also reported by Haarstad and Ludvigsen (2007) to explain why, out of 445 samples of shallow groundwater collected near agricultural fields, farm wells, and public waterworks in Norway over ten years (1995–2004), only one sample from waterworks was contaminated by glyphosate and only one farm well by AMPA. As suggested by Van Stempvoort et al. (2014), notwithstanding the widespread use of glyphosate, this herbicide may result in detectable groundwater contamination only at specific sites or areas or times (e.g. relative to herbicide application events).

The occurrence of glyphosate and AMPA in groundwater has been reported in several European countries (France, Denmark, the Netherlands, Spain, Hungary, Portugal, Ireland, Italy, Sweden, Poland, Switzerland, and Norway), American countries (Canada, the United States, Mexico, Brazil, and Argentina), Asian countries (China and Sri Lanka), and Oceania regions (New Zealand and American Samoa). Considering all monitoring studies, remarkable spatial and temporal variability in glyphosate and AMPA occurrence in groundwater can be observed (Table 3). These differences are likely due to the combined effects of pedology and geology, hydrology, climate, land management, and the timing of herbicide application. In Denmark, Malaguerra et al. (2012) analysed data from the Danish National Borehole Database over the last few decades to predict the susceptibility of drinking water to pesticide contamination and define the

338 dominant mechanisms that contribute to the pollution of the wells. The frequency of detection was 9.30 and
339 8.40% for glyphosate and AMPA, respectively. The detection frequency and concentrations of glyphosate
340 and AMPA were related to the depth of the well, geology, and redox conditions. In particular, glyphosate
341 concentration was negatively correlated with well depth, whereas for AMPA, no correlation was found. The
342 authors found that aerobic conditions that often occur in the presence of thick layers of permeable sediments,
343 such as sandy layers, may facilitate rapid glyphosate degradation. In contrast, in confined aquifers
344 delimited by clay aquitards, where anoxic conditions are more likely to prevail, glyphosate degradation
345 could be slower. The presence of aerobic conditions in an unconfined aquifer is not a rule, and it may depend
346 on the nature and thickness of the unsaturated zone. In contrast, Hakoun et al. (2017) found that impervious
347 clay aquitards might provide better protection than the unconfined aquifer because they can act as hydraulic
348 barriers by impeding or delaying the downward vertical transfer of polluted water to the confined
349 groundwater. However, there is still the possibility of lateral transfer of more recent groundwater and
350 pollutants from the unconfined to the confined area, enhanced by the pumping sites (Hakoun et al. 2017).
351 Malaguerra et al. (2012) found that with increasing distance of the well from the stream, the concentration
352 and occurrence of glyphosate and AMPA in groundwater tended to decrease. The negative correlation
353 between stream distance and compound occurrence was much more significant for glyphosate and AMPA
354 than for the other pesticides analysed. Especially in agricultural areas, the greater pesticide concentration and
355 occurrence in wells close to the streams may be related to the recharge of riparian groundwater by stream
356 water infiltration, containing high glyphosate and AMPA concentrations derived from surface runoff in
357 riparian zones. In addition, water flow in streams and rivers and population density were identified as other
358 factors influencing well pollution. High stream flow and low population density may result in lower
359 glyphosate and AMPA concentrations in streams due to dilution. Moreover, less permeable sandy sediments
360 in riparian areas can hinder the infiltration of surface water that recharges groundwater and flows to nearby
361 pumping wells.

362 The relationship between water table depth and glyphosate and AMPA detection in groundwater has been
363 investigated. Lutri et al. (2020) observed that the shallow water table depth might be a key factor
364 contributing to the high frequency of glyphosate and AMPA detection in groundwater. In Argentina, Mas et
365 al. (2020) observed a higher detection frequency of glyphosate and AMPA in hand-dug wells with a shallow

water table (27% for glyphosate and 46% for AMPA) than in boreholes where the water table was deeper than 50 m (17% for glyphosate and 11% for AMPA). Moreover, the soil of the region where the hand-dug wells were sampled was fine-textured and well-structured, causing preferential flow to become an important pathway. Furthermore, as Haarstad and Ludvigsen (2007) highlighted, the combination of shallow table depth and the vicinity of agricultural fields may pose a greater risk of groundwater contamination compared to that of small agricultural streams.

Some studies emphasized the relationship between well depth and detection of glyphosate and AMPA in groundwater (Van Stempvoort et al. 2014, 2016). Van Stempvoort et al. (2014) monitored the occurrence of glyphosate and AMPA in urban riparian groundwater collected near five streams in Canada from June to October 2009. Glyphosate and AMPA were found in 13.2 and 11.7% of the samples, respectively, with a maximum concentration of 0.04 µg/L for glyphosate and 2.87 µg/L for AMPA. The sporadic occurrence of glyphosate and AMPA in shallow groundwater is consistent with other studies (Börjesson and Torstensson 2000; Kjær et al. 2011), which indicates that these molecules are less likely to be detected at greater depths because microbial degradation and sorption in the subsurface tend to attenuate their residues. Because the groundwater was close to the stream, it is also likely that infiltration of stream water with elevated concentrations of these molecules occurred, especially at sites where the detection frequency of glyphosate was higher, indicating another possible pathway for contamination of groundwater. Van Stempvoort et al. (2016) investigated the occurrence of glyphosate and AMPA residues in shallow groundwater in an agricultural catchment in Ontario, Canada, from October 2010 to November 2013. They observed that 75% of glyphosate detection and 100% of AMPA detections were in very shallow groundwater (less than 10 m deep), and no glyphosate was detected below 17.8 m. In contrast, Sjerps et al. (2019) detected glyphosate up to a depth of 65 m. The little or no retardation, limited biodegradation, and prolonged application could explain the detection of Sjerps et al. (2019) at this great depth. Van Stempvoort et al. (2016) pointed out that glyphosate and AMPA were not always at the shallowest depth in cases where they were detected. Therefore, significant mobility probably occurs within the shallow subsurface, mainly as lateral flow, especially in shallow sand aquifers but also as downward transport accompanied by the continuous recharge of infiltrated rainfall or irrigation water. The importance of glyphosate mobility by lateral flow in the shallow saturated zone was first introduced by Kjær et al. (2011). This transport pathway involves mobility through

394 natural macropores and is enhanced when a tile drain system is present because of the gradients created by
395 inter-drain mounding of the water table during the high-flow condition after the rainfall event. Another
396 concept is mentioned in the work of Van Stempvoort et al. (2016), that is, the role of residence time in
397 indicating whether groundwater is vulnerable to pollution. Van Stempvoort et al. (2016) observed that the
398 seeps made up of locally recharged groundwater, which has short groundwater residence times (on the order
399 of weeks to months), could be more susceptible to contamination by glyphosate and AMPA, because of the
400 reduced time available for the attenuation of contaminants. Aquifers confined by semipermeable layers or
401 aquitards and made of fine-grained materials tend to have a longer travel time (on the order of decades), a
402 characteristic that confers better protection from pollutants than shallow unconfined aquifers, which tend to
403 have shorter residence times (Smith et al. 2016).

404 The hydrogeological features which influence the presence of glyphosate and AMPA in groundwater and
405 surface water were also evaluated by Lutri et al. (2020). They investigated glyphosate and AMPA
406 concentrations in 19 well water samples collected in an agricultural area of Córdoba province (Argentina) in
407 November 2017. They detected glyphosate and AMPA in 15.8% of the samples at a concentration range of
408 1.3 to 2.0 µg/L for glyphosate and 1.5 to 3.1 µg/L for AMPA. It is interesting to note that the detection
409 occurred in areas where the water table was shallow (less than 4 m deep). The hydrogeological and
410 hydrodynamic characterisation of groundwater allowed the authors to relate the aquifer vulnerability to
411 hydraulic gradient, hydraulic conductivity, and flow rate because low values of these parameters determine
412 low groundwater velocity, which in turn results in a low potential for dilution and an increased risk of
413 contamination. This does not agree with the findings of McManus et al. (2014) and Montoya et al. (2019),
414 who stated that pesticide detection is more likely to occur in higher transmissivity aquifers with high yield
415 and regional importance than in poor or only locally important aquifers.

416 Contrary to what has been found in previous studies, Okada et al. (2018) found no correlation between water
417 table depth and glyphosate and AMPA concentration in groundwater collected from windmills or electrical
418 pumps at 14 farms located in southeast Pampas, Argentina. Their results showed that 24% and 33% of the
419 groundwater samples were contaminated by glyphosate and AMPA, respectively, with high maximum levels
420 of glyphosate (8.5 µg/L) and AMPA (1.9 µg/L). Grouping the sampling sites based on the water table depth
421 (≤ 4 , 4–8, and ≥ 8 m) and analysing the relationship between water table depth and glyphosate and AMPA

occurrence in groundwater, the authors concluded that water table depth might not be the main factor involved in glyphosate and AMPA occurrence in groundwater.

The relationship between soil and aquifer characteristics and the occurrence of glyphosate in groundwater was also investigated by Abrantes et al. (2010). They evaluated the occurrence of different pesticides in groundwater, surface water, sediments, and fish tissue samples from a lake environment (Lake Vela, Portugal). Groundwater samples were collected from two wells located in the drainage basin of the lake during June and October 2004. Glyphosate was detected in all groundwater samples at concentrations ranging from 1.87 to 3.11 µg/L. The levels of glyphosate in groundwater were quite high and well above the European groundwater quality standard (0.1 µg/L), indicating a potential public health problem for residents. As the authors discussed, the presence of glyphosate in groundwater at such significant concentrations could be related to site-specific soil and aquifer characteristics, such as the sandy texture of the soil, with high permeability and low organic matter content, and the shallow depth of groundwater. Higher concentrations were detected in October for both wells, which could be associated with the increased leaching from the nearby agricultural fields to groundwater promoted by the autumn rainfall events. These results indicate that concentrations of glyphosate in groundwater may be affected by natural precipitation amounts (Székács et al. 2015).

The groundwater recharge process and its seasonality are fundamental to understanding potential groundwater pollution (Robins, 1998). To determine the times of the year in which aquifers are most vulnerable, the distribution, intensity, and duration of the recharge events need to be considered. As observed by Montoya et al. (2019), groundwater recharge is closely related to the temporal and spatial distribution of precipitation over a given region, but it also depends on the soil texture. Soils with coarser texture have a smaller field capacity and higher infiltration than finer-texture soils, resulting in greater groundwater recharge and increased risk of pesticide leaching through the soil profile. Montoya et al. (2019) assessed the groundwater vulnerability to herbicide pollution of the Quaternary aquifer system in the semiarid Pampas Plain, Argentina, using the generic and pesticide DRASTIC model. They identified high vulnerability regions as regions with shallow water tables, highly permeable soils, the prevalence of sandy components in the vadose zone, high intensity of agricultural activity, and positive water balance in the considered period of time. The DRASTIC pesticide model was tested using herbicide concentration data from groundwater.

450 Glyphosate was detected only in one well out of 95, at a concentration of 0.67 µg/L; consistent with the
451 vulnerability predicted by the model, the polluted well was located in a farm with high inputs of herbicides
452 situated in the plain sandy region of the study area.

453

454 3.3 Relationship between groundwater contamination and pollution source

455 Distinguishing the origin of pollution is not always straightforward, as glyphosate is widely used for weed
456 control in agricultural and urban environments. In addition, AMPA has more than one parent compound
457 because it can originate either from glyphosate (Borggaard and Gimsing 2008) or various phosphonates
458 (Struger et al. 2015).

459 Van Stempvoort et al. (2014) assessed the source of the AMPA detected in urban riparian groundwater in
460 Canada (glyphosate metabolite or wastewater sources, such as detergents and other phosphonates). For this
461 purpose, they used a wastewater tracer, acesulfame, and determined the correlation of AMPA concentrations
462 with those of glyphosate and acesulfame. The maximum concentrations of AMPA at each sampled reach
463 (0.55, 0.18, 2.87, and 0.13 µg/L in the first, second, third, and fourth catchment, respectively) were
464 significantly higher than those of glyphosate (0.04, 0.02, 0.01, and 0.03 µg/L in the first, second, third, and
465 fourth catchment, respectively), which could suggest wastewater as a primary potential source of AMPA.
466 However, their results showed a strong correlation between glyphosate and AMPA concentrations in
467 groundwater ($\rho = 0.754$ and 0.749 , in the first and second catchment, respectively) and only a negligible
468 correlation between acesulfame and AMPA concentration ($\rho = 0.258$ and 0.201 , in the first and second
469 catchment, respectively). Therefore, the authors concluded that the AMPA detected in groundwater is likely
470 derived mainly from glyphosate degradation rather than wastewater sources.

471 In Catalonia (Spain), Sanchís et al. (2012) conducted an extensive monitoring campaign from 2007 to 2010,
472 in which 139 groundwater samples from 69 wells located in 11 different sampling sites were collected during
473 the application season and analysed for glyphosate concentration. All but one investigated area presented a
474 high impact from intensive agriculture and were rated as high-risk areas for water pollution. Glyphosate was
475 detected in 47% of the samples, with average concentrations per site ranging from 0.097 µg/L to 0.41 µg/L,
476 which is higher than the European groundwater quality standard of 0.1 µg/L. Their results showed that
477 higher concentrations were associated with sampling carried out immediately after glyphosate application in

the area. The authors observed that more contaminated sites were located in the regions of thriving agricultural activities. Olivo et al. (2015) pointed out a relationship between the vicinity of the pollution source and the detected concentration. They observed that the two groundwater samples (out of 13) with the highest glyphosate concentration (6.80 and 1.52 $\mu\text{g/L}$) were collected from wells located in agricultural areas where the herbicide was used. Spatial differences in glyphosate and AMPA occurrence in groundwater could also be related to the crop. Analysing glyphosate and AMPA in groundwater and surface water in agricultural areas in 10 Chinese provinces, Geng et al. (2021) observed different detection frequencies in relation to the proximity to different crops. They found the highest detection frequency in the groundwater samples close to soybean (5.3% for both glyphosate and AMPA), followed by rice (3.2% for both glyphosate and AMPA), maize (0.3% for both glyphosate and AMPA), and vegetables (0.7% for glyphosate and 0% for AMPA), whereas no detection was observed in the samples close to wheat, apple, pear, sunflower, and sugarcane.

As mentioned above, glyphosate is mainly used for agricultural purposes, but it has been extensively deployed by public and private institutions for non-agricultural purposes as well, such as weed control in urban areas or along roadways and railways. The retention potential of these areas is low; therefore, glyphosate applications on these hard surfaces for maintenance purposes can be a significant source of pollution, creating concerns regarding the contamination of groundwater. In this regard, it is noteworthy that Sanchís et al. (2012) detected the highest concentration of glyphosate (2.57 $\mu\text{g/L}$) at a site where agricultural activity was only moderate, and only in a specific year (2010), which made it quite easy for them to attribute it to the use of this herbicide for non-agricultural applications in that period (weed control in urban and industrial areas).

Börjesson and Torstensson (2000) and Ramwell et al. (2004) explored the impact of a specific non-agricultural application of glyphosate on groundwater contamination. In a study conducted by Börjesson and Torstensson (2000), degradation in soil and occurrence in groundwater of glyphosate and AMPA were studied after glyphosate application for weed control on a Swedish railway embankment at three different rates: 1080 (regular application rate), 2160, and 6480 g/ha. Although some mobility of glyphosate and AMPA downward into the embankment was detected at the regular application rate, no glyphosate and AMPA were found in groundwater sampled 1.5 m below surface. This result is in agreement with Ramwell

et al. (2004), who did not find glyphosate above the LOD in groundwater samples taken from 1.5–2 m deep piezometers when glyphosate was applied at an application rate of 1080 g/ha on a railway embankment in England. At 2160 g/ha, traces of glyphosate and AMPA (0.05–0.10 µg/L) were found by Börjesson and Torstensson (2000); from the sampling performed two weeks after the application, higher concentrations were detected (0.12 and 0.31 µg/L for glyphosate and 0.30 µg/L for AMPA) due to preferential flows. A significant amount of glyphosate and AMPA were observed in all samplings when the railway embankment was treated with 6480 g/ha of glyphosate (maximum values of 1.42 µg/L for glyphosate and 0.81 µg/L for AMPA, both detected 166 days after application). Considering the favourable degradation and sorption behaviour of glyphosate, Börjesson and Torstensson (2000) and Ramwell et al. (2004) concluded that the application of glyphosate for weed control on railway embankments does not lead to significant environmental impacts when used at regular dosages. However, attention must be paid to drawing conclusions based on persistence. Indeed, as shown in Table 1, the wide range of half-life values in soil reported in the literature for both glyphosate and AMPA can be a cause for concern when interpreting studies intended to monitor the occurrence of glyphosate in groundwater. In this sense, it would be useful to base the considerations about glyphosate half-life on data obtained through more standardised approaches, such as the OECD guideline. Among the dissipation studies conducted following the OECD 307 guideline (OECD 2002a), Bento et al. (2016) in an Argentinean loess soil found DT50 values of glyphosate ranging from 1.5 days (saturated soil at 30 °C in the presence of light) to 53.5 days (soil at 20% water holding capacity at 5 °C in the presence of light). In a work aiming to study on glyphosate fate associated with plant residues in clay-loam soil, Mamy et al. (2016) obtained DT50 values in the range 9.4–26.2 days. In Colombian sandy loam soil, Muskus et al. (2020) observed a glyphosate DT50 ranging from 6.1 days (30 °C, pH 5.5, total organic carbon 3%) to 20 days (10 °C, pH 7, total organic carbon 3%–5%). In a study aiming to investigate the fate of glyphosate in water-sediment microcosms according to the OECD 308 guideline (OECD 2002b), Wang et al. (2016) observed a DT50 of glyphosate in the water-sediment system for 15 days and quick glyphosate partitioning from the water compartment to the sediments. The experimental values of DT50 can be compared to the predicted values obtained with the quantitative structure property relationship models, which were developed based on theoretically derived molecular descriptors. Ghasemi and Zolfonoun (2012) estimated a DT50 value for glyphosate of 18.1 days with the support vector machines (SVM) approach and

534 of 12.0 days with the radial basis function neural network approach. A DT50 of 9.5 days was predicted by
535 Samghani and Fatemi (2016) via the SVM approach. These values are within the range of experimental
536 DT50 values reported above.

537 538 3.4 Seasonal variations in glyphosate and AMPA occurrence and concentration

539 A combination of factors, such as application timing, agronomic practices, and weather conditions, can
540 contribute to seasonal variations in glyphosate and AMPA occurrence in groundwater. A seasonal trend in
541 the contamination of groundwater by glyphosate and AMPA, related to the application timing of glyphosate
542 (before summer crop emergence, as is common in Canada), was identified by Van Stempvoort et al. (2016).
543 The authors, analysing four years of seep data (2010–2013), observed a peak in glyphosate concentration in
544 June, followed by a gradual decline through the summer and fall, which was consistent with the seasonal
545 trend observed for surface water. The trend observed for AMPA, which prevailed in September, indicated
546 that most glyphosate had already degraded to AMPA. The application timing in addition to agronomic
547 practices may be responsible for differences in glyphosate and AMPA occurrence in groundwater. As
548 observed by Van Stempvoort et al. (2016), interannual differences in glyphosate and AMPA trends in certain
549 seeps may also be related to crop rotations within the recharge areas of the groundwater. Examples of how
550 seasonal/interannual variation in glyphosate occurrence and concentration in the groundwater could be
551 related to crop rotations and agricultural practices can be found in the literature. Monitoring glyphosate
552 concentration in five wells in two agricultural areas in the north of Argentina, Mas et al. (2020) observed a
553 decrease in glyphosate detection frequency in the 2015/16 season (50%) compared to the 2014/15 season
554 (6%). This difference was partly attributed to the type of crop and the modification of weed management
555 practices. Regarding the crop, the authors report that during the 2015/16 season, there has been an increase
556 of more than 100% in the area sown with wheat, which implies a lower use of herbicides than winter fallow.
557 Regarding the influence of weed management practices, the authors report a downward trend of applied
558 doses of glyphosate in recent years due to the emergence of resistant weeds and the diffusion of spray spot
559 systems. In Argentina, Santa Fe Province, Demonte et al. (2018) detected an increased occurrence of
560 glyphosate and AMPA traces in groundwater during the spring and summer seasons, which were related to
561 the agricultural practices in the study region. Direct sowing of soybean planted between October and

January, without soil tillage, is a diffused technique. To prepare a clean seedbed, farmers often rely on pre-emergence applications of glyphosate. Similarly, Okada et al. (2018) found that as a result of herbicide application, there was significant seasonal variation in glyphosate concentration in groundwater, with the highest concentration detected from April to August and the highest detection frequency from April to June. The detection frequency decreased to less than 90% in the following months, evidencing the short-term duration of shallow groundwater contamination by glyphosate. However, the same study revealed that AMPA concentrations did not differ between seasons, and there was no direct relationship between the presence of glyphosate and AMPA in groundwater. Moreover, whereas glyphosate concentrations and detection frequencies in groundwater were strongly associated with the time at which glyphosate concentration in soil was the highest, AMPA concentration in groundwater was not related to the concentration in the soil. This is in agreement with the findings of Van Stempvoort et al. (2014, 2016), who found that the presence of AMPA in groundwater may be mainly linked to in situ degradation of previously leached glyphosate during the course of the season, rather than to AMPA leaching from topsoil. The degradation of glyphosate to AMPA in groundwater has been documented by Crowe et al. (2011), who found that, after the application of glyphosate to *Phragmites australis* along a beach, glyphosate concentration in the groundwater declined exponentially with a half-life of 3.5 days due to both degradation and flushing.

Pazikowska-Sapota et al. (2020) observed an increase in the concentration of glyphosate and AMPA in groundwater in response to intense rainfall events after the application period. This study was conducted to assess the risk of various pesticides used in agriculture in the coastal area of the Puck commune (Pomeranian Voivodeship region, Poland). The selected area is an important agricultural region in which pollution of agricultural origin constitutes an increasing concern for the environment of Puck Bay and public health. Among the four samples of groundwater collected by four piezometers during and after the period of intensive application of pesticides (from March to August 2018), only one sample collected in August had detectable concentrations of glyphosate and AMPA (0.02 and 0.11 µg/L for glyphosate and AMPA, respectively). The same pattern was observed in surface water samples from drainage ditches, where detectable concentrations of glyphosate and AMPA were obtained only in August. Despite the reduced mobility of glyphosate and AMPA in the tested soils, the weather conditions, dry in July but with intense

590 precipitation in August, would probably have washed away these molecules from the soil, transporting them
591 to surface water and groundwater via either runoff or leaching.

592 The relationship between rainfall and detection/concentration of glyphosate and AMPA in groundwater was
593 also observed by Geng et al. (2021), Mas et al. (2020), and Rendón-Von Osten and Dzul-Caamal (2017). In
594 particular, the latter observed that heavy rainfall shortly after glyphosate application poses a higher risk for
595 glyphosate to move to the groundwater. In this study, glyphosate residues in groundwater, bottled drinking
596 water, and urine of subsistence farmers from various localities in the Hopelchén municipality (Mexico).
597 Glyphosate was detected, at concentrations up to 1.41 µg/L in 90% of the groundwater samples collected
598 from the eight investigated sites. All but one sampling locations were situated in the agricultural areas. The
599 site where glyphosate concentration was the lowest was situated in an urban area. The authors attributed the
600 widespread occurrence of glyphosate in groundwater to the widespread use of this herbicide and the nature
601 of the soil. The studied soil was karstic with a good structure and macropores, which may enhance
602 glyphosate leaching to groundwater via preferential flow. Moreover, heavy rainfall shortly after glyphosate
603 application posed a higher risk of glyphosate transport to the groundwater. In addition, Kjær et al. (2005)
604 observed that glyphosate leaching is related to single rainfall events, and it is limited to the first months after
605 the application, decreasing gradually over time. The situation for AMPA is different. Because AMPA is
606 retained more strongly and for longer in the soil, leaching occurs over a more extended period than
607 glyphosate.

608 A different situation was observed by Ruiz-Toledo et al. (2014), who investigated glyphosate concentrations
609 in wells for domestic or agricultural use during two sampling campaigns conducted over six months, which
610 included the dry and rainy seasons in the region. The wells were located near crops and naturally protected
611 areas in Chiapas in a tropical region of southern Mexico. The authors found that well samples had
612 significantly higher glyphosate concentrations in the dry season than in the rainy season. Similarly, Reynoso
613 et al. (2020) detected higher concentrations of glyphosate in groundwater in the dry seasons (autumn and
614 winter, average and maximum concentrations of 1.18 and 3.17 µg/L, respectively) than in the rainy seasons
615 (spring and summer, average and maximum concentrations of 0.46 and 1.64 µg/L, respectively) in
616 Tenampulco, Mexico. The detection of higher concentrations in the dry season than in the rainy season
617 appears controversial because, as discussed above, rain would seem to facilitate the mobility and leaching of

glyphosate from the field to groundwater. Therefore, this kind of seasonal trend seem to be related to other non-climatic factors such as sowing period and pesticide application timing, as hypothesised by Reynoso et al. (2020). Very high concentrations of glyphosate have been reported for some wells in the work of Ruiz-Toledo et al. (2014), and the maximum concentration detected was 18.43 µg/L. These results were higher than those of another study conducted in Mexico by Rendón-Von Osten and Dzul-Caamal (2017). The high concentrations observed by Ruiz-Toledo et al. (2014) appear to be motivated by the fact that the sampling sites were close to the fields of glyphosate-resistant soybean, where glyphosate is heavily used. Moreover, the high phosphate content in the soils of the study region reduces the extent of glyphosate adsorption because of the competition with phosphate, increasing the risk of leaching into groundwater (Sprankle et al. 1975; de Jonge et al. 2001; Gimsing and Borggaard 2002; Gimsing et al. 2004a, 2007).

628

3.5 Relationship between glyphosate and AMPA occurrence and concentration in groundwater

To understand the relationship between the parental compound and its metabolite in groundwater, Battaglin et al. (2014) and Okada et al. (2018) evaluated the ratio between AMPA and glyphosate concentrations (AMPA ratio):

$$\text{AMPA ratio} = ([\text{AMPA}] / ([\text{glyphosate}] + [\text{AMPA}])) \times 100, \quad \text{Eq. (1)}$$

The value of the AMPA ratio provides some insights into the glyphosate source, fate, and transport in the environment (Battaglin et al. 2014). A recent or proximal glyphosate input is indicated by lower values, whereas a longer residence time or distance between input and detection is reflected in higher values. Battaglin et al. (2014) observed that, in groundwater, AMPA tended to occur at a higher concentration than glyphosate. They detected AMPA without glyphosate in 17.9% of the samples, but glyphosate was detected without AMPA in only 2.3% of the sample. Groundwater samples had a median AMPA ratio of 100%, with an interquartile range of 70–100%. This indicates the long residence time or long distance of this hydrological setting from the source application. As also observed by Van Stempvoort et al. (2014), the residence time can significantly affect the ratio of AMPA to glyphosate concentration in groundwater. Indeed, as glyphosate degrades, the AMPA ratio increases over time because AMPA is generally more persistent than glyphosate (Feng and Thompson 1990; Simonsen et al. 2008).

645 Similarly, Okada et al. (2018) observed a higher detection frequency of AMPA in groundwater compared to
646 glyphosate. Of the 81 groundwater samples analysed, 19 samples contained only AMPA (100% AMPA
647 ratio), 10 samples contained only glyphosate (AMPA ratio equal to zero), and only 9 samples contained both
648 molecules. The median AMPA ratio was 80%, with an interquartile range of 0–100%. As suggested by
649 Kolpin et al. (2006), the higher mobility and persistence of AMPA could explain the detection of AMPA
650 when no glyphosate is present in groundwater. Owing to the absence of a concomitant occurrence, and
651 because the average glyphosate concentrations were higher than the average AMPA concentrations, the
652 authors did not find a significant correlation between glyphosate and AMPA concentrations in groundwater.
653 In contrast to soil and sediment, AMPA concentrations were positively correlated with glyphosate
654 concentrations. Moreover, the results of the National Water-Quality Assessment Program in the United
655 States (Scribner et al., 2007), the data from the Dutch Groundwater Monitoring Network (Schipper et al.
656 2008), and the National Report on pesticides in water in Italy (ISPRA, 2018) concur with results from
657 previous studies that found that AMPA occurs more frequently and at similar or higher concentrations than
658 glyphosate.

659 Conversely, Geng et al. (2021) observed a median AMPA ratio in groundwater of 36% with an interquartile
660 range of 12–65% and a strong correlation between AMPA and glyphosate concentration (Pearson correlation
661 $r=0.887$, $p=0.008<0.01$). Of the 649 samples analysed, glyphosate and AMPA were detected in six samples,
662 but glyphosate was detected without AMPA in only one sample. The authors attributed the observed
663 association between AMPA and glyphosate in groundwater to the soil processes in which glyphosate is
664 readily degraded into AMPA by soil microorganisms and leached into groundwater (Bento et al. 2016).

665

666 3.6 Comparison with other hydrologic settings

667 Numerous studies have analysed glyphosate (and, more rarely, AMPA) in groundwater and other hydrologic
668 settings such as rivers, lakes, ponds, ditches, wetlands, springs, tile-drainage water, runoff water, soil water,
669 and oceans (Grunewald et al. 2001; Kjær et al. 2005; Candela et al. 2010; Crowe et al. 2011; Mörtl et al.
670 2013; Battaglin et al. 2014; Ruiz-Toledo et al. 2014; Székács et al. 2015; Primost et al. 2017; Pinto et al.
671 2018; Gunarathna et al. 2018; ISPRA 2018; Okada et al. 2018; Sjerps et al. 2019; Welch et al. 2019;
672 Pazikowska-Sapota et al. 2020; Correia et al. 2020; Lutri et al. 2020). Mörtl et al. (2013) did not observe a

673 statistically significant difference in glyphosate concentrations between surface water ($0.422 \pm 0.271 \mu\text{g/L}$ on
674 average) and groundwater ($0.537 \pm 0.224 \mu\text{g/L}$ on average) collected in agricultural and industrial areas in
675 Békés county (Hungary) in 2010, after a rainy period. Similarly, Welch et al. (2019) found comparable
676 glyphosate concentrations in groundwater and surface water at sites where both groundwater and surface
677 water samples were collected.

678 In contrast, the National Report on Pesticides in Water in Italy (ISPRA 2018) reported a higher frequency of
679 detection of glyphosate and AMPA in surface waters (47.7% and 68.6%, respectively) than in groundwater
680 (15% and 23.1%, respectively), in 2016. Likewise, Scribner et al. (2007) and Battaglin et al. (2014) in the
681 United States, and Okada et al. (2018) detected both glyphosate and AMPA more frequently in surface
682 waters (wetlands, ponds, and lakes) than in groundwater. Battaglin et al. (2014) attributed this to the fact that
683 glyphosate in surface waters is more closely associated with the application sources and the longer time from
684 the application to the sampling in groundwater than in surface waters, giving glyphosate and AMPA the most
685 opportunity to degrade. Regarding concentration, Lutri et al. (2020) found that surface water presented a
686 higher median value than groundwater for both glyphosate and AMPA because of the high value detected in
687 the ditch. This suggests that the direct exposure of ditches to runoff from the treated field could make this
688 environmental compartment very susceptible to pollution, specifically when herbicide application coincides
689 with a rainy period. However, in the cases where glyphosate and AMPA were detected, Lutri et al. (2020)
690 found lower glyphosate and AMPA concentrations in stream water (one glyphosate detection out of three
691 samples with a concentration of $0.20 \mu\text{g/L}$ and no AMPA detections) than groundwater (three samples out of
692 19 with detectable glyphosate and AMPA at concentrations ranging from 1.2 to $2.0 \mu\text{g/L}$ for glyphosate and
693 from 1.5 to $3.1 \mu\text{g/L}$ for AMPA). The authors hypothesized that the observed situation could be attributed to
694 a lower dilution capacity of the groundwater compared to the stream water.

695 Similarly, in the study of Gunarathna et al. (2018), AMPA was detected in 45% of groundwater samples at
696 concentrations of $2\text{--}11 \mu\text{g/L}$, but it was never detected in surface water. Conversely, the authors detected
697 higher concentrations of glyphosate in surface water ($28\text{--}45 \mu\text{g/L}$, with 100% of the samples having a
698 detectable concentration of glyphosate) than in groundwater (trace levels in the range $1\text{--}4 \mu\text{g/L}$ reported for
699 all the samples). Groundwater samples were collected from shallow wells adjacent to the treated fields,
700 whereas the surface water samples came from small lakes located downstream of the fields, receiving runoff

701 water from the fields. The authors emphasized that, considering the downstream locations of the lake and the
702 vicinity to agricultural fields, the glyphosate transport with surface runoff to these environmental
703 compartments may be particularly important.

704 The distance from the application source to the monitored point, along with the dispersion and dilution
705 phenomena, determined a completely different situation in the study conducted by Crowe et al. (2011). In
706 this field study, a glyphosate-based herbicide was applied to *Phragmites australis* along a beach on the shore
707 of Georgian Bay, Canada, and glyphosate and AMPA concentrations in groundwater and lake water were
708 analysed. They found that glyphosate and AMPA concentrations in the lake water were typically lower than
709 the concentrations in the groundwater because of the dispersion of contaminants during transport with
710 groundwater flow and the dilution of groundwater with lake water when discharged into the lake.

711 According to Welch et al. (2019), submarine groundwater discharge could constitute a significant pathway
712 for glyphosate transport from coastal aquifers into the ocean, representing a potential threat to the marine
713 ecosystem. This study was conducted in a 2 km² watershed in American Samoa, using glyphosate as a tracer
714 to investigate the role of groundwater in the transport of pesticides to streams and coastal oceans. By
715 combining field investigations with MODFLOW model-derived groundwater discharge (Harbaugh et al.
716 2000), the authors found that submarine groundwater discharge of glyphosate was slightly less than 1 g/d,
717 with near-ocean groundwater concentrations of 0.16–0.30 µg/L. Although the concentrations found are not
718 likely to affect coral reef fertilisation or settlement, simultaneous exposure to glyphosate and other
719 chemicals, such as the components of glyphosate-based formulations, could result in increased toxicity to the
720 reef (Diu 2016).

721

722 3.7 Risk management measures

723 The information presented in this review highlights the presence of detectable groundwater contamination in
724 several countries worldwide. In numerous cases, concentrations exceeding the European groundwater quality
725 standard, which is the most conservative, were found. This indicates a potential risk to human health and the
726 ecosystem. Therefore, understanding the processes controlling glyphosate and AMPA mobility in a soil-
727 sediment-water environment is essential for risk management and for the development of measures to
728 mitigate groundwater contamination.

729 The European Union has established a set of rules for the sustainable use of pesticides within the Directive
730 2009/128/EC (European Parliament and the Council of European Union 2009) to decrease the risks and
731 impact of pesticide use on human health and the environment. Based on the available data on the behaviour
732 and occurrence of glyphosate and AMPA in groundwater, some precautionary measures are proposed here.
733 Some risk management measures that are proposed in this section have already been incorporated in existing
734 regulation or can be easily implemented in certain schemes by making minimal changes.

735 Considering risk mitigation, it is important to focus on the application of glyphosate on structured soils with
736 low organic matter and clay content as well as on sites with a shallow water table. Among the numerous
737 actions that promote the sustainable use of pesticides, the current regulations recommend reducing or,
738 whenever possible, eliminating pesticide use in areas for the withdrawal of drinking water, and establishing
739 protected areas to safeguard this groundwater (European Parliament and the Council of European Union
740 2000). As proposed by Swartjes and Van der Aa (2020), the elimination or minimization of pesticide use in
741 groundwater protection areas could be extended by prohibiting or limiting glyphosate usage on specific soils
742 that are prone to glyphosate and AMPA leaching in groundwater protection areas, such as soils with low
743 contents of organic matter and clay and sites with a shallow water table. In these cases, alternative methods
744 of weed management to the use of glyphosate should be considered and adopted whenever possible. In this
745 regard, Directive 2009/128/EC encourages integrated pest management and measures to promote low
746 pesticide-input pest management. Moreover, financial incentives to reward glyphosate-free approaches in
747 groundwater protection areas could emphasise farmers' proactive adoption of best management practices.

748 If alternative solutions are not applicable, glyphosate application timing should be carefully evaluated, and
749 doses should be calibrated based on the actual infestation (weed species, density, and development stage).
750 Moreover, it is crucial to follow preventive measures and implement agroecology principles for weed
751 management to reduce weed density and favour the competition of the crop as much as possible. Regarding
752 the application timing, it is essential to avoid glyphosate applications immediately before heavy rainfall,
753 especially in soils with high hydraulic conductivity, to limit the risk of leaching. Raising awareness about the
754 weather conditions that would result in a higher risk of pesticide leaching is one of the objectives of training
755 for professional users, distributors, and advisors instituted by Directive 2009/128/EC. Through training,
756 professional users can be informed about various other measures to minimise risks to the environment.

Moreover, the application of decision-support systems and early warning systems regarding weather conditions and the associated leaching risk in the case of glyphosate treatment are considered to have significant potential.

The effect of competition between glyphosate and phosphate is highly dependent on soil type (Padilla and Selim 2020), but responsible inorganic phosphorus application in the field can be advised because exceeding recommended thresholds may remobilize a fraction of soil-bound herbicides, making glyphosate more likely to leach through the soil towards groundwater. Moreover, glyphosate use for weed control in urban areas or along roadways and railways should be thoroughly reconsidered, and low environmental impact products and techniques (such as mechanical, flame, and steam weeding) should be preferred, where possible. In this sense, the installation of geotextiles for protecting the ballast and preventing the growth of weeds seems to be a promising technique.

Long-term planning and timely mitigation measures can guarantee good groundwater status in a broad sense. It is clear that the sustainability of glyphosate use, when it comes to groundwater pollution, cannot merely refer to compliance with legal limits. Rather, it must be based on an overall assessment of the environment and the ability of ecosystems to respond to anthropogenic stressors and to restore previous conditions, or at least ecologically sustainable conditions.

773

4. Conclusions

The present study highlights the detection of glyphosate and AMPA in groundwater in several countries of the world, which, in several cases, exceeds the European groundwater quality standard (0.1 µg/L), indicating a potential risk for human health and the ecosystem.

The main factors determining the risk of groundwater contamination by glyphosate and AMPA are summarized in Figure 3. The applied doses have a significant role in determining possible contamination. Heavy rainfall shortly after the application of glyphosate poses a high risk of its transport to groundwater. Application timing, agronomic practices, and weather conditions can determine the seasonal trends of glyphosate and AMPA occurrence in groundwater.

783 Most authors agree in attributing an essential role to preferential flows in favouring glyphosate and AMPA
784 transport to groundwater. High concentrations of phosphorus in the soil could hinder glyphosate and AMPA
785 adsorption to iron and aluminium oxides and hydroxides in the soil, thus favouring lixiviation.

786 Some authors agree that there is an inverse relationship between the groundwater depth and the occurrence
787 and concentration of glyphosate and AMPA in groundwater, but further studies are required to clarify the
788 importance of this factor. Clay aquitards overlying confined aquifers might offer better protection to
789 groundwater than unconfined aquifers by impeding or delaying the downward vertical transfer of polluted
790 water. Moreover, in confined aquifers, the longer groundwater residence time provides more time for the
791 attenuation of contamination through filtration, adsorption, degradation, and dilution, reducing the risk of
792 contamination of the water supply.

793 The proximity to agricultural fields where glyphosate is applied is a risk factor for groundwater
794 contamination but also the proximity to streams contaminated by glyphosate and AMPA, whose water could
795 infiltrate in the saturated zone, especially if groundwater is shallow and close to areas where glyphosate is
796 used. In this case, it becomes even more important to implement runoff mitigation measures and introduce
797 limitations in glyphosate use on hard surfaces, even in non-agricultural areas.

798 In several examined studies, AMPA was detected more frequently and at higher concentrations than
799 glyphosate. Very little information is available about the origin of AMPA when this metabolite is detected in
800 groundwater; therefore, future research should be conducted to quantify the relative importance of different
801 sources of AMPA (glyphosate and phosphonates) in groundwater.

802 In order to safeguard groundwater, the doses applied in agriculture should be reduced by integrating with
803 non-chemical weed control and appropriate crop rotation and, at the same time, measures to mitigate diffuse
804 contamination (such as buffer strips) and point contamination (such as biobed) should be applied. Moreover,
805 glyphosate use should be limited in all contexts where alternatives exist. This would allow for the possibility
806 of its use in situations in which alternatives are not practicable or convenient (such as conservation tillage
807 and railways).

808 We believe that the findings presented in this review could enhance the current understanding of the
809 relationship between glyphosate and AMPA groundwater contamination risk and both hydrogeological
810 characteristics and agricultural practices. This knowledge can help governments and public authorities

811 recognise groundwater vulnerability and undertake localised investigations to better understand the situation
812 when a higher risk is identified. Moreover, increased awareness could guide governments in defining risk
813 management measures and mitigation actions to improve the sustainability of agricultural practices through
814 targeted management programs.

815

816

817 CRediT author statement

818 Laura Carretta: investigation, writing - original draft.

819 Roberta Masin: writing - review & editing.

820 Giuseppe Zanin: conceptualization, writing - review & editing, supervision.

821

Draft

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Draft

1190 Tables

1191 Table 1. Main chemical and toxicological properties of glyphosate and AMPA.

	Glyphosate	AMPA
Chemical structure		
Molecular mass (g/mol)	169.1	111
Water solubility at 20 °C (mg/L)	10500	1466561
Dissociation constant (pKa)	2.34 ^a	–
GUS leaching potential index	-0.29	0.04
DT50 (lab studies) (days)	1.0 – 67.7	39.0 – 330.7
DT50 (field studies) (days)	5.7 – 40.9	283.6 – 633.1
K _f (mL/g)	9.4 – 700	10.0 – 1570
Mammals - Acute oral LD50 (mg/kg)	> 2000	8300

1192 ^a pKa(2) = 5.73.

1193 Source: Lewis et al. (2016)

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1195 Table 2. Limits and threshold values for glyphosate in groundwater and drinking water

Reference	Country/Union	Water type	Item	Value (µg/L)
World Health Organisation 2017	WHO	Drinking water	Guideline	900
European Parliament 2015	European Union	Drinking water	Limit	0.1
European Union 2006	European Union	Groundwater	Limit	0.1
Norwegian Ministry of Health and Social Affairs 2001	Norway	Drinking water	Threshold value	0.1
The Swiss Federal Council 1998	Switzerland	Groundwater used for drinking water	Limit	0.1
Health Canada 2019	Canada	Drinking water	Guideline	280
U.S. Environmental Protection Agency 2009	USA	Drinking water	Limit	700
SEGOB. Productos y servicios 2015	Mexico	Drinking water	Limit	10
Brasil. Ministry of Health 2016	Brazil	Drinking water	Limit	500
Argentinean National Guidelines for Human Consumption (ANGHC) 2003	Argentina	Drinking water	Guideline	300 (expressed as glyphosate isopropylamine)
Ministry of Health PRC 2006	China	Drinking water	Limit	700
General Administration of Quality Supervision Inspection And Quarantine PRC and China National Standardization Management Committee 2017	China	Groundwater	Threshold value	≤ 0.1 , class I (for various uses) ≤ 140 , class II (for various uses) ≤ 700 , class III (for centralized drinking water sources and industrial/agricultural water) ≤ 1400 , class IV (for agricultural and industrial waters; if properly treated, as drinking water) > 1400 , class V (for other uses, not as drinking water source)

1197 Table 3. Reports of glyphosate and AMPA occurrence (detection frequency, maximum concentration, and median concentration) in groundwater collected from
 1198 published literature. Articles are grouped by geographical areas (Europe, North America, South America, Asia, and Oceanian continent) and then by country. ND =
 1199 not detected; NR = not reported; NA = not analysed.

Reference	Spatial location	Site description	Number of samples	Time of collection	Depth of groundwater sampled (m below ground surface)	Glyphosate LOD and LOQ ^a (µg/L)	AMPA LOD and LOQ (µg/L)	% of glyphosate detection in samples	% of AMPA detection in samples	Maximum glyphosate concentration observed (µg/L)	Maximum AMPA concentration observed (µg/L)	Median glyphosate concentration observed (µg/L)	Median AMPA concentration observed (µg/L)
Horth and Blackmore 2009	Europe	Various sites in different European countries: ≥8925 for glyphosate; ≥7678 for AMPA	≥36298 samples for glyphosate; ≥28254 samples for AMPA	Years 1993-2009	Various	LOD = 0.01-0.4; LOQ = 0.01-0.4	LOD = 0.01-0.4; LOQ = 0.01-0.4	~1.3	~1.7	24	19	NR	NR
Kjær et al. 2005	Denmark (Jyndevad, Estrup, and Faardrup)	A site with coarse sandy soil and two sites with loamy soils, with tile drain system	NR	August 1999 - June 2002	5	LOD = 0.01; LOQ = NR	LOD = 0.01; LOQ = NR	NR	0	0.093	ND	NR	ND
Malaguerra et al. 2012	Denmark (Zealand + west part of Jutland)	Data about active drinking water wells obtained from the Geological Survey of Denmark and Greenland (GEUS)	816 for glyphosate, 799 for AMPA	Years 1984-2012	2.8 - 304	LOD = 0.01; LOQ = NR	LOD = 0.01; LOQ = NR	Zealand: 9.3 Jutland: 0	Zealand: 8.4 Jutland: 0	NR	NR	<LOQ	<LOQ
Schipper et al. 2008	The Netherlands	Samples collected at the national scale (9 provinces) and at regional scale	771	Year 2006	5, 10, and 25	LOD = NR; LOQ = NR	LOD = NR; LOQ = NR	0.32	3.2	NR	NR	<LOQ	<LOQ
Sjerps et al. 2019	The Netherlands and Flanders	Samples from 127 locations in the Netherlands + routine monitoring data from ten water companies over the years 2010 - 2014	90	May 2006 - 2016	≤250 m	LOD = NR; LOQ = NR	LOD = NR; LOQ = NR	68.2	29.8	NR	NR	NR	<LOQ

Reference	Spatial location	Site description	Number of samples	Time of collection	Depth of groundwater sampled (m below ground surface)	Glyphosate LOD and LOQ ^a (µg/L)	AMPA LOD and LOQ (µg/L)	% of glyphosate detection in samples	% of AMPA detection in samples	Maximum glyphosate concentration observed (µg/L)	Maximum AMPA concentration observed (µg/L)	Median glyphosate concentration observed (µg/L)	Median AMPA concentration observed (µg/L)
Candela et al. 2010	Spain (Maresme region)	Wells located in irrigated and non-irrigated plot under no-tillage farming	9 in the irrigated and 5 in the non-irrigated plot	September 1994 - December 1994 + February 1995 - May 1995	5.5	LOD = 0.15; LOQ = NR	LOD = 0.1; LOQ = NR	0	0	ND	ND	ND	ND
Sanchis et al. 2012	Spain (Catalonia)	69 wells located in 11 different sampling sites, the majority in agricultural areas	139	May to September 2007, 2008, 2009, and 2010	NR	LOD = 0.0032; LOQ = 0.0096	NA	47	NA	0.409	NA	<LOQ	NA
Mörtl et al. 2013	Hungary (Békés county)	14 sampling sites in agricultural and industrial areas	36	September 2010	NR	LOD = 0.12; LOQ = NR	NA	100	NA	0.98	NA	0.50	NA
Székács et al. 2015	Hungary	Samples collected in the frame of different monitoring projects in Hungary and watercourses in neighbouring countries	NR	Years 1990–2015	NR	LOD = 0.12; LOQ = NR	NA	50 ^b 27 ^c	NA	0.98 ^b 0.242 ^c	NA	NR ^b ; <LOQ ^c	NA
Abrantes et al. 2010	Portugal (Lake Vela).	Two wells located in the drainage basin of the Lake Vela (48% agricultural areas)	4	June 2004 - October 2004	NR	LOD = NR; LOQ = NR	NA	100	NA	3.11	NA	2.56	NA
Pinto et al. 2018	Portugal	Four sites across Portugal	4	NR	NR	LOD = 0.35; LOQ = 1	LOD = 0.10; LOQ = 1	0	0	ND	ND	ND	ND

Reference	Spatial location	Site description	Number of samples	Time of collection	Depth of groundwater sampled (m below ground surface)	Glyphosate LOD and LOQ ^a (µg/L)	AMPA LOD and LOQ (µg/L)	% of glyphosate detection in samples	% of AMPA detection in samples	Maximum glyphosate concentration observed (µg/L)	Maximum AMPA concentration observed (µg/L)	Median glyphosate concentration observed (µg/L)	Median AMPA concentration observed (µg/L)
Grunewald et al. 2001	Germany (Saxony)	Two agricultural areas in the catchment of the reservoir Radeburg II	NR	August 1998- January 1999	1.7	LOD = 0.05; LOD = NR	LOD = 0.05; LOD = NR	0	0	ND	ND	ND	ND
ISPRA 2020	Italy	Various monitoring points in 11 Italian regions	434 and 435 monitoring points for glyphosate and AMPA in 2017; 785 and 702 monitoring points for glyphosate and AMPA in 2018	Years 2017- 2018	Various	LOD = NR; LOQ = 0.1 µg/L in 2017 and 0.01 µg/L in 2018	LOD = NR; LOQ = 0.1 µg/L in 2017 and 0.01 µg/L in 2018	17.5 in 2017; 11.7 in 2018	23.2 in 2017; 7.1 in 2018	1.98 µg/L in 2017; 2.0 µg/L in 2018	0.87 µg/L in 2017; 3.2 µg/L in 2018	<LOQ in 2017; 0.01 µg/L in 2018	<LOQ in 2017; 0.013 µg/L in 2018
McManus et al. 2014	Ireland	159 monitoring points (springs, drilled boreholes, and wells) across Ireland, in agricultural and non-agricultural areas	845	Years 2007- 2008	NR	LOD = 0.01; LOQ = NR	NA	8	NA	>0.01 & <0.1	NA	<LOQ	NA
Swedish National environmental monitoring of pesticides, 2020	Sweden	Wells located four model catchments, mostly in agricultural areas	888	Years 2004 - 2018	3 - 6	LOD = 0.005 - 0.1; LOQ = 0.025 - 0.06	LOD = 0.015 - 0.5; LOQ = 0.05 - 0.2	3.04	1.8	0.18	0.13	<LOQ	<LOQ
Börjesson and Torstensson 2000	Sweden	Groundwater below a railway embankment to which RoundupBio was applied	38	May 1998 - October 1999	1.5	LOD = 0.05; LOQ = 0.1	LOD = 0.05; LOQ = 0.1	42	42	1.42	0.81	<LOQ for application rate 3 and 6 L/ha; 0.38 µg/L for application rate 18 L/ha	<LOQ for application rate 3 and 6 L/ha; 0.23 µg/L for application rate 18 L/ha
Pazikowska-Sapota et al. 2020	Poland (Puck Bay, Pomeranian Voivodeship)	Four piezometers located at three agricultural land plots belonging to two farms	4	February 2018 - September 2018	NR	LOD = NR; LOQ = 0.2 µg/L	LOD = NR; LOQ = 0.2 µg/L	25	25	0.021	0.11	<LOQ	<LOQ

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Ramwell et al. 2004	United Kingdom	750×6 m railway embankment. Samples taken from 4 piezometer nests with 4 piezometers each.	58	September 1999	1.5 – 2	LOD = 0.1; LOQ = NR	NA	0	NA	ND	NA	ND	NA
Hanke et al. 2008	Switzerland	Ten sites throughout Switzerland, in both agricultural and urban areas	10	Summer 2006	NR	LOD = 0.0005; LOQ = 0.0018	LOD = 0.0001; LOQ = 0.0005	0	0	ND	ND	ND	ND
Poiger et al. 2017	Switzerland	14 sites in locations with high vulnerability in 2010 and 2011; 8 sites in 2006, 2007, and 2012	141 samples in 2010 and 2011; 24 samples in 2006, 2007, and 2012	2010 and 2011	NR	LOD = NR; LOQ = 0.005	LOD = NR; LOQ = 0.005	1.4 in 2010-2011; 0 in 2006, 2007, and 2012	NR in 2010-2011; 0 in 2006, 2007, and 2012	0.025	0.65	<LOQ	<LOQ
Haarstad and Ludvigsen 2007	Norway	Farm wells and public waterworks throughout Norway	5 samples from waterworks and 8 samples from farm wells	Years 1999-2000	0.15 - 110	LOD = 0.01; LOQ = NR	LOD = 0.01; LOQ = NR	20 ^d	12.5 ^e	0.1 ^d	0.02 ^e	<LOQ	<LOQ
Smith et al. 1996	Canada (Newfoundland)	Three water wells at three electrical substations	3 samples for the 1 st substation ; 8 samples for the 2 nd and 3 rd substation	July 1994 - October 1994	NR.	LOD = NR; LOQ = NR	NA	0 for the 1 st and 2 nd substations; 100 for the 3 rd substation	NA	45	NA	ND for the 1 st and 2 nd substations; 17.5 µg/L for the 3 rd substation	NA
Crowe et al. 2011	Canada (Wasaga Beach Provincial Park, Ontario)	A beach on the southern shore of Georgian Bay, where glyphosate was applied on <i>Phragmites australis</i>	65	October 2009 - November 2009	From 0 to 0.5 m	LOD = 0.02; LOQ = 0.05	LOD = 0.06; LOQ = 0.18	NR	NR	12.5	0.62	<LOQ	<LOQ

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Van Stempvoort et al. 2014	Canada (Burlington, Barrie, and Jasper)	Riparian groundwater collected from five streams, in urban areas	281	June 2009 - October 2009	0.25 - 1 m	LOD = 0.001 - 0.01; LOQ = NR	LOD = 0.05 - 0.06; LOQ = NR	13.2	11.7	0.042	2.87	<LOQ	<LOQ
Van Stempvoort et al. 2016	Canada (Nottawasaga River, Ontario)	Shallow groundwater in a catchment dominated by agriculture	400	October 2010 - November 2013 ^f	0.1 - 38	LOD = 0.002 - 0.01; LOQ = 0.006 - 0.03	LOD = 0.002 - 0.06; LOQ = 0.006 - 0.03	10.5	5	0.663	0.698	<LOQ	<LOQ
Kolpin et al. 2004	United States (Iowa)	86 municipal wells representing the major aquifer types in Iowa	86	Year 2001	NR	LOD = 0.05; LOQ = NR	LOD = 0.05; LOQ = NR	0	0	ND	ND	ND	ND
Scribner et al. 2007	United States	Different studies conducted in various sites across the United States	873	Years 2001-2006	NR	LOD = 0.1 - 0.02; LOQ = NR	LOD = 0.1 - 0.02; LOQ = NR	7.8	15.2	4.7	2.6	<LOQ	<LOQ
Battaglin et al. 2014	United States (38 states + District of Columbia)	Shallow and deep groundwater sampled from various wells across the United States, in agricultural and non-agricultural areas	3732	Years 2001-2010	NR	LOD = 0.02; LOQ = NR	LOD = 0.02; LOQ = NR	5.8	14.3	2.03	4.88	<LOQ	<LOQ
Ruiz-Toledo et al. 2014	Mexico (Soconusco region, State of Chiapas)	23 sampling sites in agricultural fields and two natural protected areas	6	February 2013 - July 2013 ^f	NR	LOD = 0.05; LOQ = 0.13	NA	100	NA	18.43	NA	0.34	NA
Rendón-Von Osten and Dzul-Caamal 2017	Mexico (Hopelchén municipality, State of Campeche)	Wells used as water sources and infiltration wells, in an agricultural area	29	NR	NR	LOD = 0.05; LOQ = 0.13	NA	90	NA	1.41	NA	1.13	NA

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Reynoso et al. 2020	Mexico (Tenampulco, State of Puebla)	5 sampling sites of which 4 groundwater wells and 1 bottled drinking water from treated groundwater	16 groundwater samples and 4 bottled drinking water samples, taken in 4 different periods of time	May 2018, August 2018, January 2019, and November 2019 ^f	NR	LOD = 0.05; LOQ = NR	NA	88 in groundwater; 0 in bottled water	NA	3.17 in groundwater	NA	0.41 in groundwater	NA
Olivo et al. 2015	Brazil (Chapecó)	13 deep wells, some of them located in a rural area with strong agricultural influence	13	NR	NR	LOD = 0.07; LOQ = 0.24	NA	38	NA	6.80	NA	<LOQ	NA
Correia et al. 2020	Brazil (Federal District and eastern Goiás)	28 springs and 14 artesian and semi-artesian wells from 20 farms in the Samambaia River sub-basin	84	February 2016 and August 2016	15 - 190	LOD = 0.38; LOQ = 1.15	LOD = 1.01; LOQ = 3.06	NR	0	11.33 µg/L (in spring water)	ND	NR	ND
de Oliveira et al. 2020	Brazil (Japarutuba River Basin)	10 wells along the river and its tributary channels near to an oil field	5	December 2018	NR	LOD = NR; LOQ = 100	NA	0	NA	ND	NA	ND	NA
Santos et al. 2020	Brazil (Dourados, Mato Grosso do Sul)	Artesian well at the campus of University of Mato Grosso do Sul	1	NR	70	LOD = 2.87; LOQ = 9.47	NA	0	NA	ND	NA	ND	NA
Pires et al. 2020	Brazil (Santarém plateau, Amazon region, Pará State)	Shallow wells close to soybean growing fields in the Santarém plateau	10	May 2017	NR	LOD = NR; LOQ = 0.2 µg/L	LOD = NR; LOQ = 0.50 µg/L	70	0	9.7	ND	3.8	ND
Primost et al. 2017	Argentina (Entre Rios Province)	Windmills at 17 farms in the Mesopotamic Pampas	17	January 2012 - March 2012	40 - 60	LOD = 0.07; LOQ = 0.22	LOD = 0.15; LOQ = 0.44	0	0	ND	ND	ND	ND

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Okada et al. 2018	Argentina (Buenos Aires Province)	Windmills or electrical pumps at 14 farms in the Austral Pampas	81	April 2015 – March 2016 ^f	from <4 to >8	LOD = 0.1; LOQ = 0.5	LOD = 0.1; LOQ = 0.5	24	33	8.5	1.9	NR (average concentration = 0.4 µg/L)	NR (average concentration = 0.1 µg/L)
Demonte et al. 2018	Argentina (Santa Fe Province, Castellanos and Las Colonias departments)	Wells in 40 dairy farms	125	Spring 2012, and Summer, Autumn and Winter 2013 ^f	Well depth: 20-25 m; phreatic levels from 2.2 to 10.3 m	LOD = 0.2; LOQ = 0.6	LOD = 0.1; LOQ = 0.2	66 (15% of quantified values)	96 (52.8% quantified values)	11.3	6.5	<LOQ	0.2
Montoya et al. 2019	Argentina (La Pampa Province)	95 wells from 16 farms in different vulnerability zones of the study area	95	NR	0-10 m in the Eastern part; 20-25 m in the central part	LOD = NR; LOQ = 0.10 µg/L	LOD = NR; LOQ = 0.30 µg/L	1	0	0.67	ND	<LOQ	ND
Lutri et al. 2020	Argentina (Córdoba Province)	Monitoring wells at 19 sites, in agricultural areas	19	November 2017	15 - 50	LOD = 0.1; LOQ = NR	LOD = 0.1; LOQ = NR	15.8	15.8	2	3.1	<LOQ	<LOQ
Mas et al. 2020	Argentina (Santiago del Estero, Bandera and Sachayoj city)	5 hand-dug wells in Bandera and 2 boreholes in Sachayoj	58 from dug well, 19 from borehole	April 2014 – June 2017 ^f	Wells: shallow; boreholes: > 50 m	LOD = NR; LOQ = 0.10	LOD = NR; LOQ = 0.13	27 in dug wells; 17 in boreholes	46 in dug wells; 11 in boreholes	10.6 in dug wells; 0.9 in boreholes	1.9 in dug wells; 0.5 in boreholes	<LOQ	<LOQ
Geng et al. 2021	China	252 sites in the agricultural basins located in 9 provinces of China	694	Between April and November during 2017–2018	From 2 to ~300	LOD = 0.05; LOQ = 0.1	LOD = 0.05; LOQ = 0.1	1.01	0.86	2.09	5.13	<LOQ	<LOQ
Jing et al. 2021	China (Golmud, Qaidam Basin)	67500 m ² medlar field (250×250 m)	9	August 2019, 15 days after the last pesticide application	1.8-1.85-1.9-2.0-2.1-2.4-2.7	LOD = 0.01; LOQ = 0.03	NA	0	NA	ND	NA	ND	NA

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Gunaratna et al. 2018	Sri Lanka (Anuradhapura District)	Shallow wells near nine agricultural fields in areas with chronic kidney disease of unknown etiology	18	NR	NR	LOD = 0.01; LOQ = 0.1	LOD = 0.01; LOQ = 0.1	100	40	4	11	3	<LOQ
Close et al. 2021	New Zealand	279 wells, of which 84% from unconfined aquifers	259	- Year 2016 (41 samples); - September – December 2018 (147 samples); - November 2019 – April 2019 (71 samples)	75% of the wells: <25 m; 15% of the wells: 25-48 m; 10% of the wells: >48m.	LOD = 1; LOQ = NR	LOD = 1; LOQ = NR	0.36	0	2.1	ND	<LOQ	ND
Hadfield 2017	New Zealand (Waikato region)	40 groundwater wells	40	Year 2017	NR	LOD = 1; LOQ = NR	LOD = 1; LOQ = NR	0	2.5%	ND	1.9	ND	<LOQ
Welch et al. 2019	American Samoa (Tutuila)	Groundwater sampled at 6 sites: 3 from stream bank sediments, 2 from coastal springs, and 1 from a public well	6	August 2016	From 0.4 to 32	LOD = 0.05; LOQ = NR	NA	100	NA	0.3	NA	NR	NA

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1201^a LOQ: Limit of quantification.

1202^b Project "Comparison of Regional Pesticide Contamination in Intensive and Ecological (Organic) Agriculture".

1203^c Project "Transnational Survey of Seasonal Pesticide Contamination in Rivers in the Carpathian Basin".

1204^d Detected only in public waterworks.

1205 ^e Detected only in farm wells.

1206 ^f Evaluation of the seasonal variability of concentrations was considered.

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1207 Figure captions

1208 Figure 1. Sources of glyphosate and AMPA in groundwater. The sources of AMPA as degradation product
1209 of amino polyphosphonates are in italics. Arrows with dotted line and arrows with double line indicate runoff
1210 and leaching, respectively; WWTP = wastewater treatment plant.

1211

1212 Figure 2. Summary of inclusion and exclusion criteria.

1213

1214 Figure 3. Summary of the main factors influencing the risk of groundwater pollution by glyphosate and
1215 AMPA. Two contrasting situations are represented, in which the combination of factors determine a high and
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Draft

Figure 1. Sources of glyphosate and AMPA in groundwater. The sources of AMPA as degradation product of amino polyphosphonates are in italics. Arrows with dotted line and arrows with double line indicate runoff and leaching, respectively; WWTP = wastewater treatment plant.

255x107mm (150 x 150 DPI)

Figure 2. Summary of inclusion and exclusion criteria.

240x160mm (150 x 150 DPI)

Figure 3. Summary of the main factors influencing the risk of groundwater pollution by glyphosate and AMPA. Two contrasting situations are represented, in which the combination of factors determine a high and low risk of groundwater pollution, respectively.

260x106mm (150 x 150 DPI)