

## Review

# Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review

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**Abstract:** The very wide use of glyphosate to control weeds in agricultural, silvicultural and urban areas throughout the world requires that special attention be paid to its possible transport from terrestrial to aquatic environments. The aim of this review is to present and discuss the state of knowledge on sorption, degradation and leachability of glyphosate in soils. Difficulties of drawing clear and unambiguous conclusions because of strong soil dependency and limited conclusive investigations are pointed out. Nevertheless, the risk of ground and surface water pollution by glyphosate seems limited because of sorption onto variable-charge soil minerals, e.g. aluminium and iron oxides, and because of microbial degradation. Although sorption and degradation are affected by many factors that might be expected to affect glyphosate mobility in soils, glyphosate leaching seems mainly determined by soil structure and rainfall. Limited leaching has been observed in non-structured sandy soils, while subsurface leaching to drainage systems was observed in a structured soil with preferential flow in macropores, but only when high rainfall followed glyphosate application. Glyphosate in drainage water runs into surface waters but not necessarily to groundwater because it may be sorbed and degraded in deeper soil layers before reaching the groundwater. Although the transport of glyphosate from land to water environments seems very limited, knowledge about subsurface leaching and surface runoff of glyphosate as well as the importance of this transport as related to ground and surface water quality is scarce.

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**Keywords:** sorption; degradation; AMPA; colloidal transport; phosphate competition

## 1 INTRODUCTION

Glyphosate [*N*-(phosphonomethyl)glycine], which is the active ingredient in Roundup and other weed-killing formulations, is a broad-spectrum, post-emergence, non-selective herbicide. It is the world's biggest-selling chemical used for weed control in agricultural, silvicultural and urban environments.<sup>1–4</sup> This wide use can very much be ascribed to high weed-killing efficiency, low toxicity to non-target organisms and apparently a very limited risk of leaching to groundwater because glyphosate seems to be inactivated in soils by strong sorption and relatively fast degradation.<sup>1,5–9</sup> Further, adding to glyphosate popularity was the introduction in 1997 of Roundup Ready™ crops, such as cotton, maize and soybeans,<sup>3</sup> which are made glyphosate resistant by incorporation of a naturally occurring, glyphosate-resistant protein.

The wide use, and hence ubiquity, of glyphosate makes great demands on glyphosate safety, i.e. the absence of any harmful environmental effect except on target organisms (the undesirable weeds). In spite of many papers<sup>5,6,8,10–12</sup> showing that glyphosate is relatively safe environmentally, recent investigations

indicate possible leaching and toxicity problems with its use.<sup>4,13–18</sup> Recent studies have also shown that soil sorption and degradation of glyphosate exhibit great variation depending on soil composition and properties.<sup>9,19–24</sup> Therefore, it is worthwhile reconsidering the fate of glyphosate in soils, including sorption, degradation and leachability. The objectives of this review are to point out the state of knowledge on glyphosate fate in soils, as well as to identify areas where more research is needed because of limited or inconclusive data. In order to place the outcome of this review in context, a few comments on the toxicological aspects of using glyphosate are first presented.

## 2 GLYPHOSATE TOXICITY

The herbicidal function of glyphosate is to prevent the plant from producing essential aromatic amino acids (phenylalanine, tryptophan, tyrosine), but, since animals are unable to produce these amino acids, they are not affected by this function.<sup>8,10</sup> Accordingly, reviews of many investigations of glyphosate toxicity on birds, dogs, fish, mice, rabbits, rats and other animals

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have shown that glyphosate is largely non-toxic; toxic effects can only be provoked by very high doses.<sup>8,10,12</sup> In addition to very low acute toxicity, these reviews also conclude that glyphosate is non-carcinogenic. Furthermore, glyphosate seems to have no or very limited detrimental effects on microbial populations and processes.<sup>5,25</sup> Accordingly, the US maximum contaminant level (MCL) of glyphosate in drinking water is  $700\ \mu\text{gL}^{-1}$ , which is higher than the MCLs for other pesticides.<sup>26</sup> However, this concentration is much higher than the European tolerable level of only  $0.1\ \mu\text{gL}^{-1}$ .<sup>27</sup> The very large discrepancy between American and European permissible levels is due to different policies. In Europe,  $0.1\ \mu\text{gL}^{-1}$  is administratively set as the upper tolerable threshold for all pesticides, while the US maximum is based on toxicity tests on glyphosate.

Recently, glyphosate has been claimed to be very toxic to amphibians under natural conditions; nearly all tadpoles were killed after 3 weeks in an outdoor pond sprayed with Roundup, and direct spraying of Roundup on land eliminated most juvenile frogs and toads after 1 day.<sup>15,28</sup> This work has been strongly criticised<sup>29</sup> because of 'the atypical application rates, unrealistic high aqueous exposure, and design limitations'; arguments that were seriously refuted.<sup>30</sup> Several studies have demonstrated toxic effects of formulations and of the additives (surfactants) used in the formulations (e.g. polyethoxylated tallowamine, POEA in Roundup), while these effects were not demonstrated with glyphosate alone.<sup>11,31,32</sup> In fact, Relyea<sup>15</sup> also mentions that the lethal impact on the amphibians could very well be attributed to POEA and not the glyphosate. It is important to note that the dispute is about possible effects of Roundup, and not of glyphosate, which is the focus of this paper. Furthermore, since aminomethylphosphonic acid (AMPA), the primary degradation product of glyphosate, seems to be equally or less toxic than glyphosate,<sup>8</sup> the use of glyphosate may be considered environmentally neutral, but toxicological problems still persist with the additives (surfactants) that are needed for glyphosate to penetrate plant cuticles.

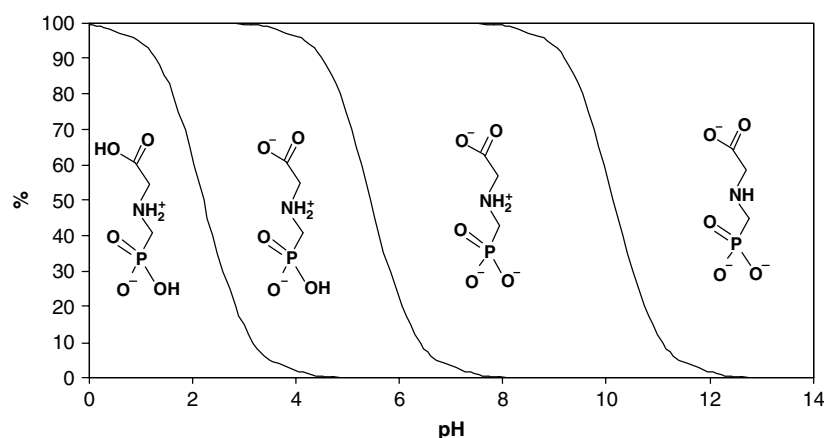
### 3 SORPTION OF GLYPHOSATE

Mobility, and hence leachability, of a compound in soil depends on its sorption characteristics, i.e. strong sorption to soil solids results almost in immobilisation, while a weakly sorbed compound can be readily leached. Compared with other pesticides, glyphosate possesses unique sorption characteristics in soil. Almost all other pesticides are moderately to weakly sorbed in soils, mainly by soil organic matter (SOM), because most of these molecules are dominated by apolar groups, i.e. aliphatic and/or aromatic carbon, and often have only one functional group.<sup>33–35</sup> In contrast, glyphosate, which is a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups), is strongly sorbed by soil minerals.<sup>9,24,36,37</sup> Accordingly, glyphosate is a polyprotic acid and forms, within the pH range of 4–8 found in most soils, mono- and divalent anions with high affinity for, in particular, trivalent cations such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ .<sup>37–39</sup> Since phosphate reacts similarly, glyphosate and phosphate may compete for the surface sites, which may affect glyphosate sorption, and hence mobility, in phosphate-rich soils.<sup>9,20,24</sup>

#### 3.1 Sorbents and factors affecting sorption

Glyphosate can only be sorbed onto variable-charge surfaces, not onto permanent-charge (negative) sites on layer silicates, as it is an anion in the relevant pH range of soils (Fig. 1). Therefore, the main soil sorption sites are found on surfaces of aluminium and iron oxides, poorly ordered aluminium silicates (allophane/imogolite) and edges of layer silicates; especially sorption by goethite ( $\alpha\text{-FeOOH}$ ) which has been shown in numerous studies.<sup>36–41</sup> Accordingly, soils enriched with these variable-charge minerals have been demonstrated to be effective glyphosate sorbents, whereas soils dominated by permanent-charge minerals such as illite, smectite and vermiculite sorb less glyphosate.<sup>7,9,20,24</sup>

Table 1 shows the amounts of glyphosate sorbed by aluminium and iron oxides and silicate clays. Very different amounts of glyphosate are sorbed by the various pure minerals, depending on the surface area



**Figure 1.** Distribution of glyphosate species as a function of pH (Bjerrum diagram). Acid dissociation constants:  $\text{pK}_{\text{a}1} = 2.22$ ,  $\text{pK}_{\text{a}2} = 5.44$  and  $\text{pK}_{\text{a}3} = 10.13$ , taken from Sheals *et al.*<sup>37</sup> The zwitterionic structure of carboxyl and amino groups is shown in the entire pH range.

**Table 1.** Glyphosate sorption at pH 7 by synthetic aluminium and iron oxides and pure, K<sup>+</sup>-saturated layer silicates

Mineral	SSA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Glyphosate sorption		Reference
		(mmol kg <sup>-1</sup> )	(μmol m <sup>-2</sup> )	
<i>Aluminium and iron oxides</i>				
Gibbsite	45	72	1.60	36
Ferrihydrite	343	635	1.85	38
Goethite	85	125	1.45	37
Hematite	33	86	2.61 <sup>b</sup>	38
<i>Clay silicates</i>				
Kaolinite 1	12	3.9	0.33	36, 42
Kaolinite 2	22	6.9	0.31	36, 42
Illite	43	5.2	0.12	36, 42
Montmorillonite	32	6.5	0.20	36, 42

<sup>a</sup> Specific surface area determined by applying the BET equation to N<sub>2</sub> sorption.

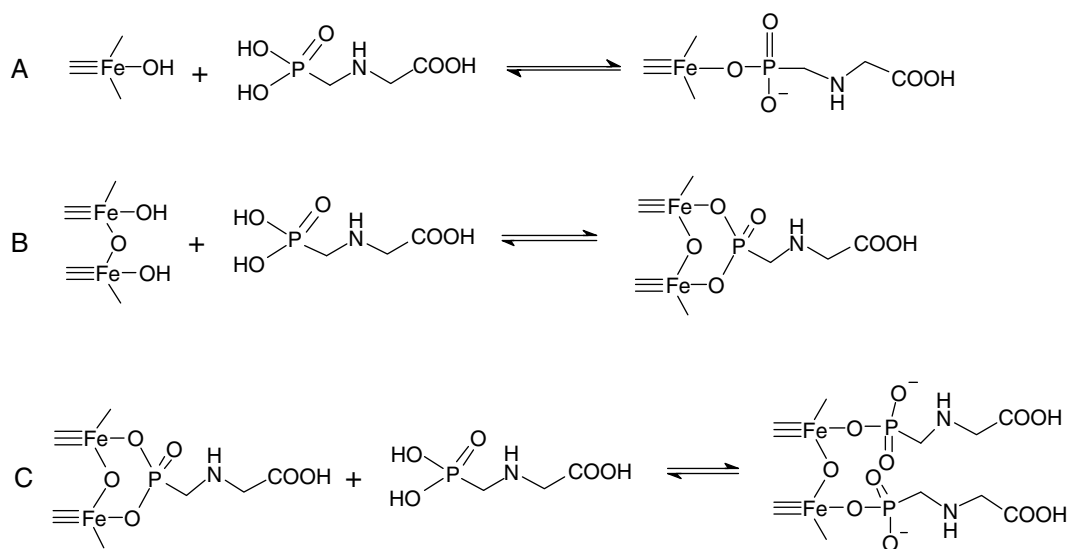
<sup>b</sup> This value is undoubtedly too high owing to inappropriate hematite synthesis, as discussed by Gimsing and Borggaard.<sup>38</sup>

and on the mineral group, resulting in sorptions of 1.45–1.85 (2.61) μmol m<sup>-2</sup> for aluminium and iron oxides, and of 0.12–0.33 μmol m<sup>-2</sup> for silicate clays. The discrepancy between the two mineral groups can be attributed to the number and distribution of sorption sites. On the oxides, plenty of sorption sites are available on various surfaces, while the layer silicates probably only possess sorption sites (OH groups) on octahedral layers exposed on mineral edges and not on the much larger planar faces.<sup>33</sup>

In addition to specific surface area and mineral group, glyphosate sorption also depends on pH. The amount of glyphosate sorbed by goethite has been found to decrease at increasing pH.<sup>37,39</sup> This is in accordance with decreased sorption of other phosphonates and phosphate at increasing pH because of increased negative charge (or lowering of positive sorbent charge) on sorbate and sorbent at higher

pH.<sup>33,42,43</sup> Glyphosate sorption by a Danish topsoil also gradually decreased when pH was raised from 6 through 7 to 8, and, in a multiple regression analysis with five soils, pH was the most important single factor for glyphosate sorption, which was negatively correlated with pH.<sup>9</sup> Decreased soil sorption of glyphosate at increasing pH has also been shown in other studies.<sup>44,45</sup> However, increasing pH by liming seems to have the opposite effect, i.e. increased glyphosate sorption at increasing pH, but this increase was ascribed to the formation of (more) glyphosate-sorbing aluminium and iron oxides at higher pH.<sup>20</sup>

Sorption of glyphosate seems to occur by ligand exchange or specific sorption by the formation of a mononuclear, monodentate surface complex at singly coordinated hydroxyl groups, although the formation of a binuclear, bidentate (bridging) surface complex at contiguous (neighbouring) singly coordinated hydroxyl groups cannot be completely ruled out.<sup>37–40</sup> The formation of these complexes on the surface of an iron oxide is illustrated in Fig. 2. As indicated, glyphosate binds through the phosphonate group in accordance with the results of attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic and atomic force microscopy (AFM) studies of the surface complexes.<sup>37,39,40</sup> In addition, a linkage between the surface and the carboxyl group has also been suggested.<sup>40</sup> However, as indicated by the ATR-FTIR analysis, the surface–carboxyl binding, if it exists, must be very weak.<sup>37,39</sup> Non-existence or extreme weakness of this bonding has been suggested by Schnürer *et al.*,<sup>46</sup> who showed that goethite-sorbed glyphosate, which is normally considered to be protected against microbial attack, can undergo decarboxylation by microorganisms leaving behind a phosphate compound, probably AMPA, on the goethite surface.

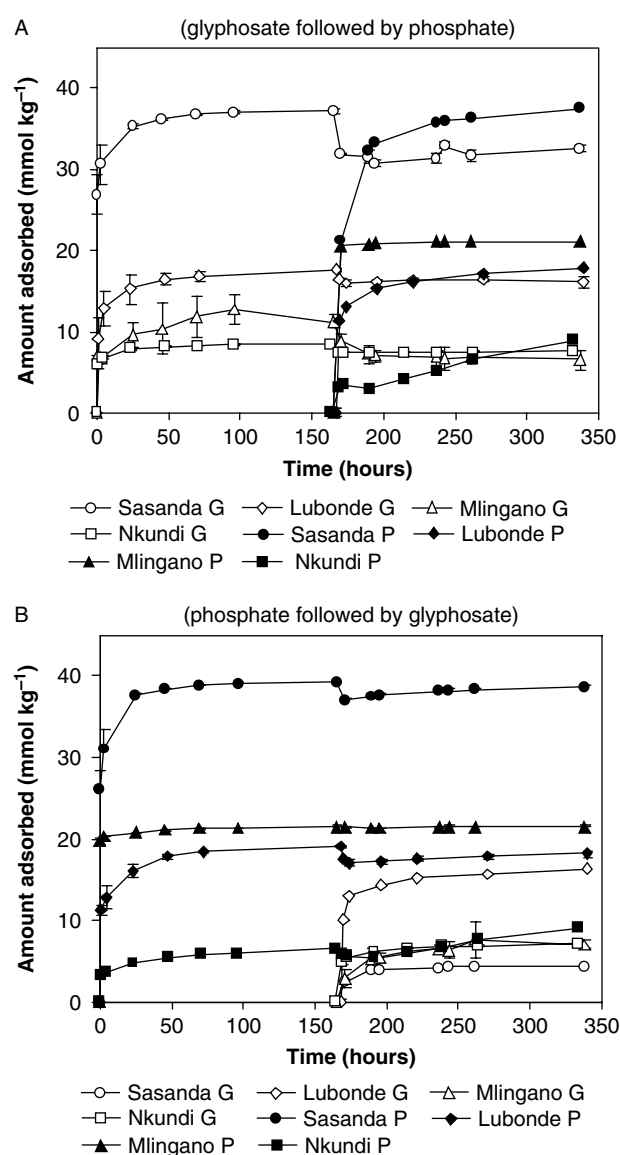


**Figure 2.** Tentative reaction schemes for glyphosate sorption by an iron oxide: A, formation of mononuclear, monodentate surface complex; B, formation of binuclear, bidentate surface complex; C, formation of dense packed mononuclear, monodentate surface complexes from binuclear, bidentate surface complex at increased glyphosate concentration. Zwitterionic structure of carboxyl and amino groups omitted.

As shown in Table 1, glyphosate sorption by the oxides amounted to 1.45–1.85 (2.61)  $\mu\text{mol m}^{-2}$ . These amounts are considerably less than the total numbers of singly coordinated (potentially sorbing) hydroxyl groups on the oxide surfaces; average iron oxides have  $\sim 3$  OH groups  $\text{nm}^{-2}$ , corresponding to  $\sim 5.0 \mu\text{mol m}^{-2}$ .<sup>33,47</sup> Accordingly, with the figures in Table 1, a mononuclear, monodentate bond between glyphosate and oxide surface will cause occupation of less than half of the singly coordinated OH groups (Fig. 2A), and even the formation of binuclear, bidentate surface complexes (Fig. 2B) will still leave some OH groups unoccupied (except on the hematite). Because glyphosate is a rather bulky molecule,<sup>41</sup> the formation of the closed-packed surface complex resulting from the reaction in Fig. 2C is considered unlikely, i.e. glyphosate seems to occupy less than half of the available surface sites.

Except for ferrihydrite, the reaction between glyphosate and the oxides and silicates in Table 1 is rather fast, and completed within a few hours.<sup>36,38,41</sup> The slower reaction with ferrihydrite has been attributed to slow diffusion into less accessible interior sorption sites.<sup>38</sup> Glyphosate sorption by soils normally consists of an initial fast sorption accounting for most uptake, followed by a slow reaction, which may continue for several days, sorbing minor amounts of glyphosate.<sup>9,24,48</sup> Initially fast and then slow sorption of glyphosate (and phosphate) is shown for four tropical soils in Fig. 3, which also exemplifies the strong influence of soil composition on glyphosate sorption. The influence of temperature on glyphosate sorption kinetics (and degradation), which may be important in relation to global warming,<sup>49</sup> seems unresolved, but the sorption rate is expected to increase at higher temperature as the rate of interactions between solutes and soil components is expected to double or triple per 10 °C increase in temperature ( $Q_{10} = 2-3$ ).<sup>33</sup>

Silicate clays have limited capacity to sorb glyphosate (Table 1), but the amounts seem to depend on the solution cation (saturating cation). Thus, decreasing sorption by montmorillonite, illite and kaolinite was found to follow the order:  $\text{Al}^{3+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Na}^+$ ,<sup>50,51</sup> the clay silicates in Table 1 were  $\text{K}^+$  saturated. The increased sorption on saturation with divalent and, in particular, trivalent cations may be explained by complex formation between interlayer cations and glyphosate.<sup>44</sup> However, this explanation only applies to montmorillonite with readily available interlayers, whereas interlayers are not readily available in illite and are lacking in kaolinite.<sup>33</sup> In contrast, Morillo *et al.*<sup>52</sup> found glyphosate sorption by montmorillonite only on external sites (Al–OH groups on edges), and the presence of  $\text{Cu}^{2+}$  caused decreased sorption owing to the formation of Cu–glyphosate complexes with lower sorption affinity than glyphosate. These and other contradictions concerning sorption dependency



**Figure 3.** Competitive sorption of glyphosate and phosphate by four Tanzanian soils, an Andisol (Sasanda), two Oxisols (Lubonde, Mlingano) and an Ultisol (Nkundi): A, glyphosate is added first, i.e. at time zero, followed by phosphate addition after 160 h; B, phosphate is added first, i.e. at time zero, followed by glyphosate addition after 160 h. Vertical bars indicate standard deviations. Reprinted from *Geoderma*<sup>24</sup> with permission from Elsevier.

on pH and order of sorption capacity of illite, kaolinite and smectite<sup>44,51,53</sup> strongly indicate that the main contribution of clay silicates to glyphosate sorption might be attributed to the OH groups on octahedral layers, i.e. to groups similar to the singly coordinated hydroxyl groups on aluminium and iron oxides.

Soil organic matter seems to play a controversial and dual role in soil sorption of glyphosate. On the one hand, investigations have shown that soil sorption of glyphosate is not, or is sometimes negatively, correlated with SOM content.<sup>7,9,48,54</sup> On the other hand, Piccolo *et al.*<sup>55</sup> reported very high glyphosate sorption by four different purified humus samples (HSs). This sorption was explained by the formation of hydrogen bonding between humus and glyphosate,<sup>55</sup> but it seems questionable that rather weak hydrogen

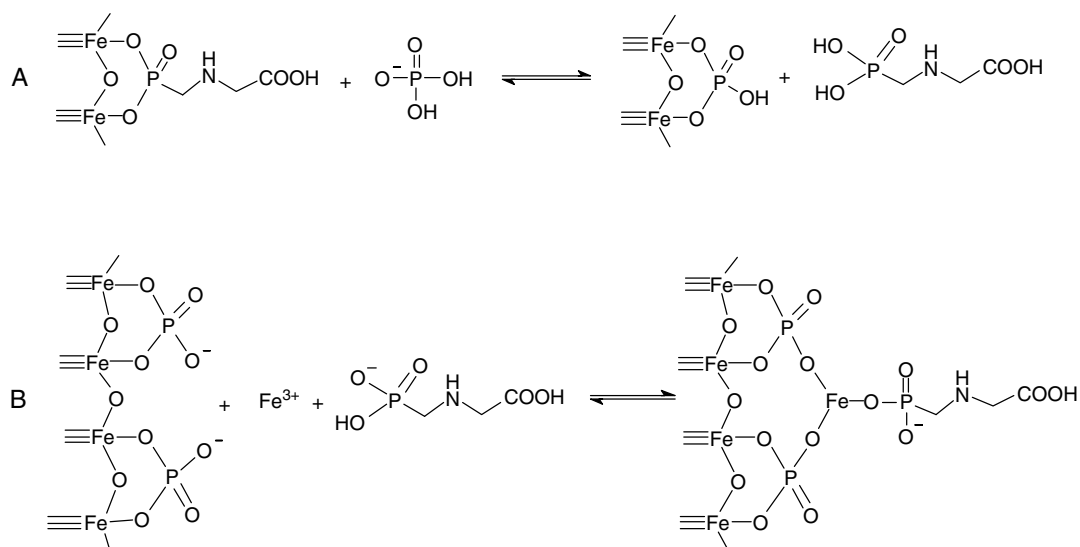
bonds can overcome the repulsion between negatively charged humus and glyphosate anions (Fig. 1). The formation of ternary humus–Me–glyphosate complexes, where Me denotes di- and trivalent metal cations in humus samples and background electrolyte (0.01 M CaCl<sub>2</sub>), is considered a more likely explanation. A comparison with phosphate, which is sorbed similarly to glyphosate (Section 3.2), indicates that SOM may have indirect effects on glyphosate sorption but in two opposite ways: (i) SOM may reduce glyphosate sorption by blocking sorption sites and (ii) SOM may increase glyphosate sorption because poorly ordered aluminium and iron oxides with high sorption capacity are favoured at higher SOM content. For phosphate, blocking of sorption sites by SOM seems only to be temporary, as it ceased after a few days, while the influence on oxide crystallinity was lasting.<sup>56</sup> Whether or not glyphosate sorption by soils is similarly affected by SOM has not been shown. Finally, incorporation of corn residues or of Bt Cry1Ac toxin had no or a negative effect on glyphosate sorption by sandy and sandy loam soils.<sup>57,58</sup>

### 3.2 Competition with phosphate

Glyphosate and phosphate are both sorbed by ligand exchange on variable-charge Al–OH and Fe–OH surface sites under the formation of strong Al–O–P or Fe–O–P bonds.<sup>40,47</sup> Competition for sorption sites between glyphosate and phosphate therefore seems obvious and may have a severe impact on glyphosate bonding, and hence leachability, especially on many agricultural soils in Europe, the USA and elsewhere that are saturated or nearly saturated with phosphate because of surplus phosphorus fertilisation over many years.<sup>59–61</sup>

Sorption of glyphosate and phosphate by goethite clearly demonstrated competition and phosphate sorption preference inasmuch as presorption of phosphate eliminated glyphosate sorption and presorbed

glyphosate was mobilised (desorbed) by phosphate addition.<sup>41</sup> The competitive reaction of glyphosate and phosphate at an iron oxide surface is illustrated in Fig. 4A. For sorption on goethite, equilibrium is almost completely shifted to the right, which, if extrapolated to soils, might indicate glyphosate leaching on phosphate-saturated soils.<sup>41</sup> Such strong competition and phosphate preference seems, however, rather unique for goethite, although sorption by gibbsite also occurred in competition with some phosphate preference.<sup>36</sup> Sorption by other iron oxides and clay silicates showed limited competition that differed from mineral to mineral.<sup>36,38</sup> In fact, the iron oxides in Table 1 displayed the whole spectrum from very strong competition and phosphate preference on goethite to little competition and phosphate preference on hematite.<sup>38</sup> These results suggest that, in addition to competitive sorption, sorption of glyphosate and phosphate may also be additive, i.e. some surface sites are common sites able to sorb both sorbates, while other sites are specific for either glyphosate or phosphate. According to this suggestion, almost all sites on goethite are common sites, whereas most hematite sites are specific; for other minerals the distribution between common and specific sites is variable but falls between these extremes.<sup>38</sup> Furthermore, in the presence of both sorbates, the sum of sorbed glyphosate and phosphate is larger than for each of the two sorbates. Thus, for hematite the glyphosate sorption capacity is 2.61 μmol m<sup>-2</sup> (Table 1) and the phosphate sorption capacity is 2.85 μmol m<sup>-2</sup>, but, in total, 4.17 μmol m<sup>-2</sup> of glyphosate + phosphate was sorbed in the presence of both sorbates.<sup>38</sup> This difference can be explained by the occurrence of two site types, common sites and specific sites. Alternatively, it may be attributed to sorption in different planes, as indicated in Fig. 4B, where glyphosate is sorbed on phosphate through a metal cation, e.g. Al<sup>3+</sup> and Fe<sup>3+</sup>, similarly



**Figure 4.** Tentative reaction schemes for sorption of glyphosate and phosphate: A, competitive sorption; B, sorption in two planes (glyphosate on phosphate). Both glyphosate and phosphate are assumed to form binuclear, bidentate surface complexes. Zwitterionic structure of carboxyl and amino groups on glyphosate omitted.

to the mechanism suggested by Nowack and Stone<sup>62</sup> for sorption of various phosphonates and phosphate.

The great variability regarding glyphosate/phosphate competition shown by pure minerals is also reflected by soils. Considerable competition is exhibited by some soils but not by others. Thus, for the four variable-charge tropical soils in Fig. 3, the allophane/imogolite-rich Sasanda soil shows rather strong competition and phosphate preference, especially when looking at the very low glyphosate sorption following phosphate sorption (Fig. 3B); probably the sorption mechanism resembles that in Fig. 4A for an iron oxide. In contrast, almost the same amount of glyphosate may be seen to be sorbed by the Nkundi soil in the absence and presence of phosphate. Similarly, five Danish soils dominated by permanent-charge minerals exhibited different extents of competition,<sup>9</sup> indicating that glyphosate/phosphate interaction is not simply a matter of variable-charge versus permanent-charge soil mineralogy. Sorption sites on soils undoubtedly behave as those on oxides, i.e. some sites are common sites exhibiting glyphosate/phosphate competition and some sites are specific for glyphosate or phosphate, but two-plane sorption (Fig. 4B) may also contribute.

Competition between glyphosate and phosphate for soil sorption sites was in fact shown shortly after launching the herbicide in 1974 by Sprankle *et al.*,<sup>50,63</sup> who concluded that the phosphate content was the most decisive factor for glyphosate sorption. Several subsequent studies have confirmed the competitive sorption of glyphosate and phosphate as well as its substantial variability on various soils.<sup>20,45,53,64,65</sup> The environmental concern in relation to glyphosate/phosphate competition is attributed to the suppressed glyphosate sorption on phosphate-enriched soil (indicated in Fig. 3B) because reduced sorption may lead to an increased risk of glyphosate leaching to the aquatic environment. As shown in Fig. 3B, the extent of suppression of glyphosate sorption on phosphate-enriched soil is time dependent, as indicated with the Lubonde soil. Considerably stronger time dependency was found for some of the Danish soils, where glyphosate sorption nearly doubled from 2 hours to 7 days for one soil with 3.1% organic carbon.<sup>9</sup> This time dependency indicates temporary blocking of sorption sites, possibly by SOM, as also shown for phosphate sorption by iron oxides with presorbed humic substances.<sup>56</sup> In soils with high hydraulic conductivity, reluctant sorption suggests increased risk of leaching of glyphosate if applied immediately before heavy rainfall, even though the soils have considerable glyphosate sorption capacity at equilibrium.

Summarising, glyphosate is sorbed in soils onto variable-charge surface sites, mainly on aluminium and iron oxides and poorly ordered aluminium silicates (allophane/imogolite), while sorption by permanent-charge layer silicates is limited. Sorption increases with increasing specific surface area of the sorbents but decreases at increasing pH. SOM does not

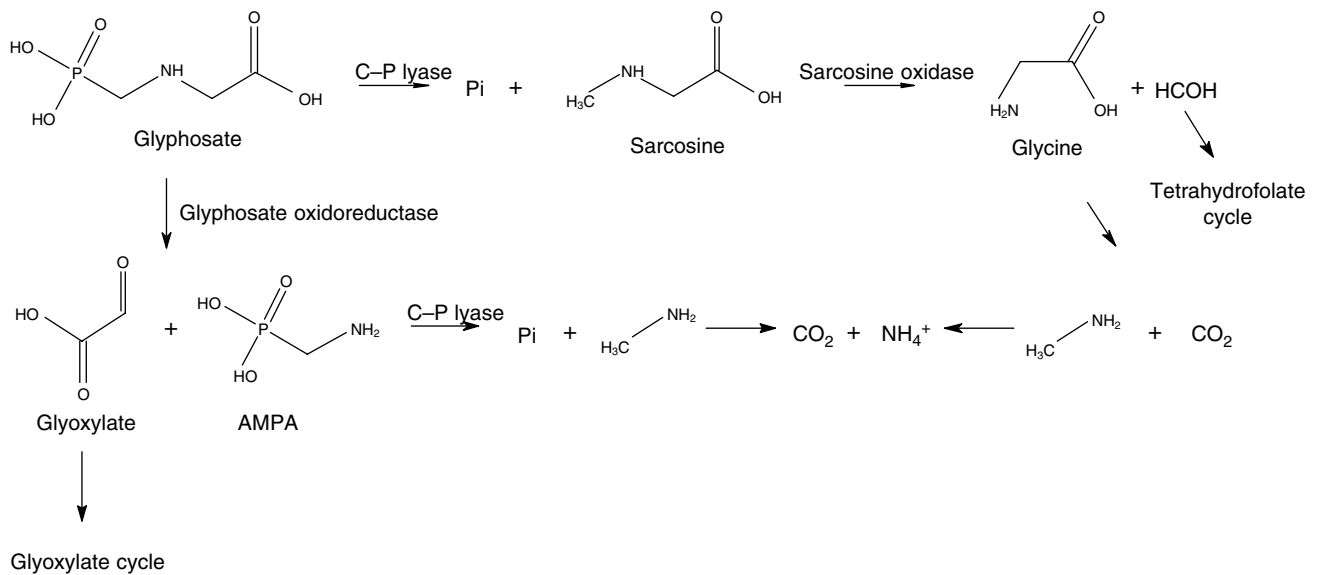
seem to sorb glyphosate but may indirectly affect glyphosate sorption, e.g. by temporary blocking of surface sites and by stabilising poorly ordered oxides with high sorption capacity. Through the phosphonate group, sorbed glyphosate is strongly bonded to singly coordinated Al–OH and Fe–OH surface sites by Al–O–P and Fe–O–P bonds, forming mononuclear, monodentate and/or binuclear, bidentate surface complexes, similarly to phosphate sorption. The similar bonding suggests competition between glyphosate and phosphate for surface sites. In fact, on application to phosphate-rich soils, reduced glyphosate sorption has been demonstrated repeatedly, but recent investigations show that the extent of reduction is strongly soil dependent. After presorption of phosphate, one soil with high glyphosate sorption capacity almost lost its ability to sorb glyphosate, while in other soils the influence of phosphate was limited. The strong, but not fully understood, soil dependency indicates that determination of glyphosate sorption, and hence leachability, in a certain soil is not simple as it seems to depend on several soil characteristics such as mineralogical composition (mineral types, contents and crystallinity), pH, phosphate content and maybe SOM.

#### 4 GLYPHOSATE DEGRADATION

Glyphosate degradation in soils has been considered to be a pure microbiological process as practically no degradation occurred in sterile soil, whereas degradation took place in non-sterile soil.<sup>16,50,66</sup> However, recently Barrett and McBride<sup>67</sup> demonstrated abiotic glyphosate degradation by the manganese oxide birnesite. In spite of this observation, the main glyphosate degradation is accomplished by various microorganisms, which, together with soil factors affecting the degradation and rate of degradation, will be considered subsequently.

##### 4.1 Degradation pathways and organisms

Microorganisms degrade glyphosate through two pathways.<sup>68–73</sup> One pathway leads to the intermediate formation of sarcosine and glycine, and the other leads to the formation of AMPA (Fig. 5). In the AMPA pathway, the first step is the cleavage of the C–N bond by the enzyme glyphosate oxidoreductase, producing AMPA and glyoxylate.<sup>2,69,72,74,75</sup> Glyphosate oxidoreductase is a flavoprotein employing FAD as a cofactor, and the mechanism probably involves the reduction of FAD at the active site by glyphosate. Under aerobic conditions, oxygen is used as a cofactor, whereas under anaerobic conditions compounds like phenazine methosulfate and ubiquinone act as electron acceptors.<sup>74</sup> The glyphosate oxidoreductase enzyme has been inserted into different plant genomes, where it is responsible for glyphosate tolerance in Roundup Ready<sup>™</sup> crops.<sup>74</sup> Glyoxylate is further metabolised via the glyoxylate cycle.



**Figure 5.** Microbial degradation of glyphosate through sarcosine or AMPA. Zwitterionic structure of carboxyl and amino groups omitted.

AMPA is cleaved to produce inorganic phosphate and methylamine, which is ultimately mineralised to CO<sub>2</sub> and NH<sub>3</sub>.<sup>2,75,76</sup> The enzyme C-P lyase is responsible for the cleavage of AMPA.<sup>77,78</sup> The C-P lyase enzyme has been extensively studied, because cleavage of the C-P bond is the critical step in the degradation of glyphosate and other phosphonates.<sup>77,78</sup> In spite of all efforts, it has not been possible to determine the precise degradation mechanism, but from studies of various alkylphosphonates it is proposed that it is a redox-dependent radical-based dephosphorylation, with the initial step being the formation of a phosphonyl radical.<sup>77</sup>

The genes encoding the degradation of phosphonates (the *phn* genes) are under the control of the Pho regulon, which means that their expression is regulated by exogenous phosphate. Thus, C-P lyase activity is induced under phosphate starvation, and microorganisms may use phosphonates as an alternative phosphorus source.<sup>77–79</sup> This is in accordance with several studies in which it has been shown that glyphosate is utilised as a phosphorus source, but not as a carbon or nitrogen source, and that phosphate affects degradation of glyphosate negatively.<sup>70–73,75,80,81</sup> However, recently microorganisms capable of utilising phosphonates, including glyphosate, as a carbon or nitrogen source even in the presence of phosphate have been isolated, and it has been found that cleaving of the C-P bond takes place even if phosphate is present.<sup>46,78,82–84</sup>

In the sarcosine pathway (Fig. 5), the initial step is the cleaving of the C-P bond by C-P lyase, producing phosphate and sarcosine.<sup>70,73,85</sup> Sarcosine is further degraded to glycine and formaldehyde by sarcosine oxidase. The formaldehyde enters the tetrahydrofolate-directed pathway of single-carbon transfers, and glycine is metabolised by the standard

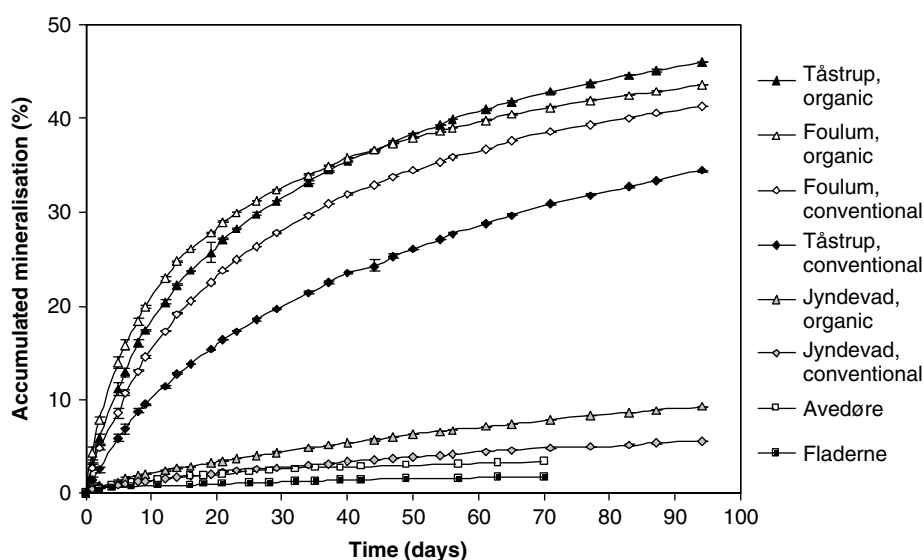
pathways.<sup>68,70,85</sup> Ultimately CO<sub>2</sub> and NH<sub>3</sub> are formed.

Up to the mid-1980s, AMPA was believed to be the major glyphosate metabolite.<sup>66,86</sup> However, in 1986 a *Pseudomonas* bacterium capable of degrading glyphosate via the sarcosine pathway was isolated, and the sarcosine pathway was suggested as unique to this bacterium.<sup>85</sup> Later it was pointed out that only two of the microorganisms that use the AMPA pathway have been isolated from sources other than industrial glyphosate-degrading effluents, whereas use of the sarcosine pathway had been found in diverse environmental and laboratory strains.<sup>73</sup> In fact, a wide variety of soil microorganisms, including bacteria, actinomycetes, fungi and unidentified microorganisms, are able to degrade glyphosate, but bacteria seem to play the leading role in glyphosate degradation.<sup>87</sup>

Whether the AMPA or the sarcosine pathway is most common in soil is not known, and it will be difficult to determine. As AMPA is often detected in soil that has received glyphosate,<sup>9,13,21,88–90</sup> this degradation pathway must be found in soil microorganisms. Sarcosine, on the other hand, has not been detected in soil, which may simply be attributed to its fast degradation, while the more resistant AMPA is strongly sorbed through the phosphonate group and protected against further microbial degradation.<sup>88,90</sup>

#### 4.2 Factors affecting degradation

Soils can exhibit great variability in their ability to degrade glyphosate (Fig. 6).<sup>21,22,86,91</sup> Some investigations indicate that glyphosate degradation is correlated with the general microbial activity.<sup>2,66,92</sup> Thus, Franz *et al.*<sup>2</sup> found the glyphosate degradation rate to be correlated with the respiration rate, and von Wirén-Lehr *et al.*<sup>92</sup> reported that the soil microbial biomass, as measured by substrate-induced heat output and total adenylate content, was correlated with glyphosate degradation. In contrast, Gimsing *et al.*<sup>19</sup> found no



**Figure 6.** Mineralisation of glyphosate in five Danish topsoil pairs (conventional and organic agriculture) measured as the accumulated mineralised glyphosate as percentage of applied glyphosate. Reprinted from *Applied Soil Ecology*<sup>19</sup> with permission from Elsevier.

correlation between glyphosate mineralisation and the general microbial activity as measured by the basal respiration or the total number of culturable microorganisms, but mineralisation was correlated with the number of *Pseudomonas* sp. bacteria. Mineralisation/degradation of glyphosate in soil has also been found to be inversely correlated with the glyphosate sorption capacity of the soil,<sup>22,89,90</sup> i.e. if sorption is strong, then the mineralisation/degradation is low, possibly because bioavailability is low. On the other hand, recently Schnürer *et al.*<sup>46</sup> have demonstrated that glyphosate sorbed to the iron oxide goethite could be degraded to AMPA and then to phosphate.

Degradation of glyphosate seems to be a cometabolic process,<sup>2,57,63,66</sup> because microorganisms are not able to use glyphosate as a carbon source<sup>73,85</sup> and because the degradation of glyphosate has been correlated with the general microbial activity of the soil.<sup>2</sup> The observation that degradation of glyphosate takes place without a lag phase in soil has also been seen as evidence for cometabolic degradation,<sup>2</sup> because the enzymes used in the degradation must be present before the application of glyphosate. However, recent studies have shown that some organisms are capable of using glyphosate as a carbon or nitrogen source.<sup>46,82,84</sup>

In a study by Gimsing *et al.*,<sup>19</sup> glyphosate mineralisation at three locations was investigated in soils that had received glyphosate previously and in soils that were organically managed and therefore had not received glyphosate for at least 15 years. As shown in Fig. 6, the mineralisation was highest in the organically managed soils (especially the Tåstrup soil), indicating that there is no adaptation to glyphosate degradation, and that mineralisation is controlled by other factors. In further support of no adaptation, maximum mineralisation in a clayey soil profile was found 1.90–2.26 m below the soil surface, i.e. at a depth where soil layers

have not been exposed to glyphosate before.<sup>22</sup> Unfortunately, manganese, which stimulates both abiological and microbiological glyphosate degradation,<sup>21,67</sup> and might explain the higher degradation rate, was not determined in this investigation.<sup>22</sup>

Degradation of glyphosate takes place under both aerobic and anaerobic conditions, although the degradation under anaerobic conditions is normally less than under aerobic conditions.<sup>66</sup> In fact, Sørensen *et al.*<sup>22</sup> found negligible mineralisation of glyphosate in anoxic soil layers. This may be important if global climatic change causes changes in soil moisture conditions as indicated.<sup>49</sup> Furthermore, global change with increased temperature will undoubtedly increase glyphosate degradation. Thus, Stenrød *et al.*<sup>93</sup> presented data for one French and two Norwegian soils showing a  $Q_{10}$  of about 2 for glyphosate mineralisation in the temperature range 5–28 °C.

Starting without a lag phase, the initial mineralisation of glyphosate in soil is rapid, corresponding to degradation of soil-solution glyphosate, followed by a gradually decreasing rate which has been attributed to rate-limiting desorption of glyphosate bonded to soil surfaces (Fig. 6).<sup>13,16,22,66,86,89,92,94</sup> Gimsing *et al.*<sup>19</sup> found that, in soils with high glyphosate mineralisation rates, the pool of iron- and aluminium-bound glyphosate decreased over time, indicating that continuous mineralisation will desorb glyphosate from this pool. Furthermore, the addition of iron or aluminium, which sorb glyphosate, significantly reduced the degradation rate.<sup>89</sup> These observations indicate the importance of sorption/desorption processes for glyphosate mineralisation in soil. The investigations also showed that the rate of degradation is very soil dependent. Thus, as exemplified in Fig. 6, more than 40% of added glyphosate was mineralised at 15 °C after 3 months in some soils, while in other soils less than 5% was mineralised under the same conditions. These percentages correspond to half-life times ( $t_{1/2}$ ,

DT<sub>50</sub>) of 100 days (Tåstrup soil) to 1000 days (Jyndevad), as estimated by a first-order rate expression. These DT<sub>50</sub> values are comparable with or somewhat higher than previously reported half-life times as compiled by Laitinen *et al.*,<sup>23</sup> which ranged from a few days to 8 months. Although it is commonly held that glyphosate is readily degraded in soils,<sup>2,8,10,57,58</sup> these results show that this is not always the case, emphasising the great variability among soils.

Even though a first-order rate expression is often used for DT<sub>50</sub> estimation, application of such simple rate expressions to glyphosate mineralisation does not always result in good fits.<sup>19,21,23,94–96</sup> In order to improve the fit, Eberbach<sup>94</sup> proposed fitting with two first-order equations, one equation describing the degradation of readily available glyphosate and the other equation accounting for less available (sorbed) glyphosate. However, even this model cannot always adequately describe degradation or mineralisation of glyphosate in soil, indicating the complexity of glyphosate degradation.<sup>19</sup> Obviously, a good description of glyphosate degradation in soils requires application of more sophisticated models that take into account sorption/desorption, diffusion processes and transition products, e.g. AMPA.<sup>21,95,96</sup>

In pure culture studies with glyphosate as the only P source, the degradation kinetics is different from degradation in soil and it has also been demonstrated that the degradation rate of glyphosate can exhibit great variation for different microorganisms.<sup>72,75,76,81,85,97</sup> In contrast to soil degradation, pure culture degradation of glyphosate starts with a lag phase with very slow degradation, followed by a gradually accelerating phase running into very fast degradation of the glyphosate, which is eventually used up. These results indicate that, although experiments with pure cultures may give useful information, e.g. about degrading potentials of different microorganisms, application of the results to soils must be done with great caution.

Phosphate can affect the mineralisation of glyphosate both by downregulating the genes encoding C–P lyase and by suppressing the uptake of glyphosate.<sup>69,72,76</sup> The two degradation pathways of glyphosate are affected differently by phosphate, because cleaving of the C–P bond is the first step in the sarcosine pathway, whereas in the AMPA pathway the cleaving of the C–P bond is the second step (Fig. 5). Accordingly, phosphate did not affect the degradation of glyphosate to AMPA by a *Flavobacterium* sp., but the degradation of AMPA was inhibited by phosphate and glyphosate was not degraded in the presence of phosphate by *Pseudomonas* sp. strain PG2982, which uses the sarcosine pathway.<sup>70,75</sup> In contrast, Pipke and Amrhein<sup>76</sup> found that *Arthrobacter atrocyaneus* did not degrade glyphosate by the AMPA pathway in the presence of phosphate, possibly owing to inhibited uptake of glyphosate. More recent studies have demonstrated the existence of microorganisms capable

of degrading glyphosate or other organophosphonates, even in the presence of high levels of phosphate.<sup>78,83,84</sup>

Studies on the effect of phosphate on glyphosate mineralisation in soil have shown that phosphate may have a positive effect, no effect or even a negative effect on mineralisation.<sup>19,89</sup> For the soils shown in Fig. 6, phosphate addition had a strong stimulating effect on glyphosate mineralisation in the soils with the slowest mineralisation rate, i.e. the Avedøre, Fladerne and Jyndevad soils, while no or negative effects were seen for the fast mineralising soils, including the Foulum and Tåstrup soils, and with negligible influence of agricultural practice, i.e. conventional versus organic farming.<sup>19</sup> Surprisingly, the content of available phosphate was highest in the most positively responding soil, the Jyndevad soil.<sup>19</sup> These discrepancies can, however, tentatively be explained if soils possess different surface sites, where some are common (competitive) and some are specific glyphosate or phosphate sites as discussed in Section 3.2. Depending on the contents of common versus specific sites in the soils, glyphosate degradation can be more or less dependent on phosphate availability, i.e. in soils dominated by common sites, which prefer phosphate, the addition of phosphate will increase glyphosate desorption and hence accelerate degradation, whereas the glyphosate degradation rate will be little affected by phosphate in soils mainly populated by specific sites. Alternatively, the different influence of phosphate on glyphosate degradation may be explained by stimulation of *Pseudomonas* by phosphate addition in the slowly mineralising soils.<sup>19</sup>

Summarising, glyphosate degradation in soils is mainly a microbiological process that can be accomplished by different microorganisms, but bacteria, in particular *Pseudomonas* sp., seem the most important. Microorganisms can use two degradation pathways: (i) through AMPA and (ii) through sarcosine. However, while the AMPA pathway is well documented, degradation through sarcosine is still a matter for dispute. Sorption is considered to decrease glyphosate degradation, but sorbed glyphosate seems not always protected against microbial degradation. Soils in general seem to degrade glyphosate, but the degradation rate can be very different from one soil to another and will increase at increasing temperature. The influence of phosphate on glyphosate degradation is very soil dependent inasmuch as available phosphate stimulates glyphosate degradation in some soils, while in other soils it has the opposite or no effect. These different effects can tentatively be explained in a similar way to the different, soil-dependent glyphosate/phosphate sorption behaviours in Section 3.2, i.e. by an assumed, but yet not proven, occurrence of two kinds of surface site comprising common sites subjected to glyphosate and phosphate competition but with phosphate preference, together with specific sites available for either glyphosate or phosphate. Alternatively, the different phosphate effect may be explained as a stimulation of

*Pseudomonas* by phosphate addition in soils with low degradation capacity.

## 5 LEACHING OF GLYPHOSATE

Transport of potentially sorbable compounds such as glyphosate and its metabolite AMPA from terrestrial to aquatic environments can occur in solution and in suspension, i.e. the compounds can be transported as solutes or cotransported bonded to soil colloids (colloid-facilitated or particle-bonded transport). Both dissolved and particle-bonded forms can be moved by leaching through the soil (subsurface runoff) and by overland flow (surface runoff). Subsurface leachates end up in drainage and groundwaters, while the direct recipients of surface-runoff-transported materials are open waters such as streams and lakes. In uniform, non-structured (apedal) soils, e.g. many sandy soils, water movement through the soil can be described as piston flow (matrix flow), while in structured (pedal) soils, e.g. many clayey soils, preferential flow bypassing more or less the soil matrix is common. Preferential pathways are macropores, including biopores and fissures/cracks between aggregates, but can also be bands of higher hydraulic conductivity such as sand bands in a clay matrix.<sup>33,98</sup>

These transport mechanisms are reviewed in this section, with emphasis on glyphosate transport.<sup>4,13,14,16–18,23</sup> By focusing on transport mechanisms and causes in relation to glyphosate sorption and degradation, it is intended to supplement and update the information given by Vereecken,<sup>7</sup> who presented a very comprehensive review on glyphosate mobility and leaching in soils, but with a different approach to experiments at laboratory, lysimeter and field scale.

### 5.1 Glyphosate in uniform (non-structured) soils

The abilities to sorb and degrade glyphosate seem to be general soil properties but are very soil dependent (Sections 3 and 4). Some soils have high glyphosate sorption capacities, while modest amounts are sorbed by other soils (Fig. 3). Similarly, glyphosate degradation is rather fast in certain soils, but slow degradation rates are also commonly seen (Fig. 6). Subsurface glyphosate leaching might therefore be expected in soils with low sorption capacity and slow degradation rate, e.g. on sandy, oxide-poor soils with high hydraulic conductivity that receive high precipitation rates, in particular when glyphosate is sprayed immediately before heavy rainfall.

The Jyndevad soil in Fig. 6 is a sandy soil with a very low mineralisation rate, and, as shown previously,<sup>9</sup> its glyphosate sorption capacity is low, indicating the risk of glyphosate leaching in that soil. However, field investigations over 2 years with analyses of drainage water after glyphosate application showed no leaching of glyphosate (or AMPA), which was attributed to the absence of macropores, i.e. the soil is non-structured

(apedal) and water moves through the soil matrix as piston flow.<sup>14</sup> In addition to matrix flow, the observed effective glyphosate retention may be ascribed to a fast reaction between soil and glyphosate, or the high hydraulic conductivity of the coarse textured soil would lead to glyphosate leaching. On the other hand, considering the low sorption and degradation rate in the Jyndevad topsoil,<sup>9,19</sup> a limited translocation of glyphosate from top- to subsoil, well above 1 m, cannot be excluded because the Jyndevad subsoil has high contents of poorly ordered aluminium and iron oxides (this soil is partly podzolised), and hence high glyphosate sorption capacity.<sup>9,14</sup> Nevertheless, the results of Kjær *et al.*<sup>14</sup> are in agreement with lysimeter (column) experiments showing no or very little glyphosate leaching in sandy soils without macropores, and hence no bypass flow.<sup>16,99,100</sup> Furthermore, the concentration of glyphosate was below the detection limit ( $<0.04 \mu\text{g L}^{-1}$ ) in drainage water samples taken 1 m below the soil surface in a sandy, non-vegetated soil sprayed with Roundup.<sup>18</sup> Laitinen *et al.*<sup>23</sup> found translocation of glyphosate from topsoil to subsoil (down to 50–70 cm below the soil surface) in one sample in a sandy soil but interpreted the result as due to translocation of glyphosate through the plants to the roots, and eventual delivery to the soil.

Glyphosate leaching has been demonstrated in uniform but very coarse-textured soil materials, such as under railway embankments, where high rates of glyphosate have been used for weed control; glyphosate concentrations above the European threshold ( $0.1 \mu\text{g L}^{-1}$ )<sup>27</sup> were reported in groundwater samples.<sup>17</sup> Glyphosate leaching can also be severe on gravelly materials, since glyphosate concentrations up to  $1300 \mu\text{g L}^{-1}$  were found in leachates from short columns packed with gravel of different particle sizes.<sup>16</sup>

Accordingly, glyphosate leaching is limited in uniform, non-structured soils without macropores, e.g. many sandy soils, and the risk of surface and groundwater pollution by glyphosate (and AMPA) is considered to be low. However, long-term use of glyphosate to control weeds on coarse-textured soil materials such as gravel may lead to glyphosate pollution of groundwater, which indicates that oxide-poor sandy soils with a shallow groundwater table may also be vulnerable.

### 5.2 Glyphosate in structured soils

Only a few studies have shown or indicated subsurface leaching of glyphosate (and AMPA) in structured soils and soil materials with macropores and bypass flow.<sup>4,13,14</sup> Of these studies, that of Kjær *et al.*<sup>14</sup> appears to be the most comprehensive and informative. In short, this study comprised the monitoring over 2 years of the precipitation concentrations of glyphosate, AMPA and bromide (conservative tracer) in drainage water samples from tile drains 1 m below the soil surface at three locations with rather typical, but contrasting, Danish, cultivated mineral soils at Estrup in mid-Jutland (a complex, structured clay soil,

Glossudalf), at Faardrup in mid-Sealand (a structured clay soil formed on calcareous till, Argiudoll) and at Jyndevad in south Jutland (a uniform, somewhat podzolised sandy soil, Dystrudept). Collection of drainage water was done by time-proportional sampling, where samples were taken at regular time intervals (1 h), and by flow-proportional sampling, where sampling was induced by drainage runoff and only activated during storm events. Total concentrations of glyphosate and AMPA in the water samples were quantified by gas chromatography–mass spectrometry (GC-MS) after acidification, concentration and formation of volatile derivatives.<sup>14</sup>

As mentioned, glyphosate and AMPA were not detected in the Jyndevad samples, while, at Faardrup, AMPA was found in some leachates in low concentrations (0.02–0.11  $\mu\text{g L}^{-1}$ ) and glyphosate in concentrations of <0.1  $\mu\text{g L}^{-1}$  on only two occasions.<sup>14</sup> In contrast, relatively strong subsurface leaching of glyphosate and AMPA occurred at Estrup, as shown in Fig. 7, for the first year (2000–2001), where glyphosate and AMPA concentrations of up to 2.1 and 0.73  $\mu\text{g L}^{-1}$  respectively were found, with means of 0.54  $\mu\text{g L}^{-1}$  (glyphosate) and 0.17  $\mu\text{g L}^{-1}$  (AMPA). The concentrations depended on mode of sampling inasmuch as flow-proportional sampling resulted in higher concentrations of both glyphosate and AMPA (but not of bromide) than time-proportional sampling (Fig. 7). In fact, more than 90% of the glyphosate and AMPA leached during the first year could be accounted for by the 11 storm events.<sup>14</sup> Similarly, Veiga *et al.*<sup>4</sup> found high leachate concentrations of glyphosate after storm events. It may also be noted that the highest glyphosate concentrations occurred in samples taken during the first heavy storm events around November after application on 13 October (Fig. 7). These results suggest fast transport of glyphosate and AMPA, presumably through macropores and colloid facilitated. The occurrence of macropores was shown by hydraulic conductivity measurements,<sup>14</sup> and the importance of colloid-facilitated transport was emphasised by De Jonge *et al.*<sup>99</sup> Furthermore, the time elapsed (~2 weeks) between glyphosate application and rainfall<sup>14</sup> is very long compared with the time needed for glyphosate sorption (Fig. 3), making the presence of free (non-colloid-sorbed) glyphosate in the leachates unlikely.

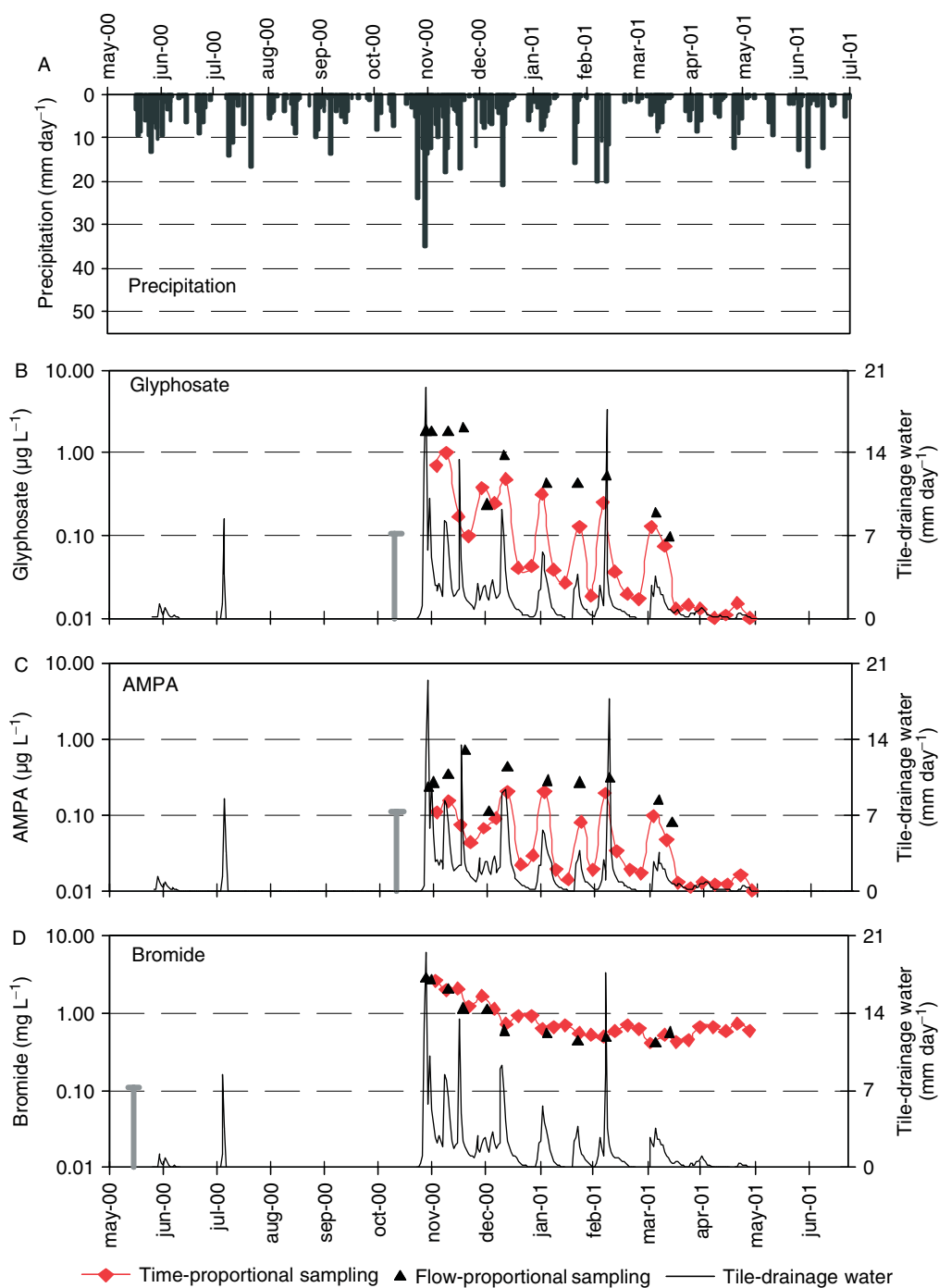
Vertical transport of glyphosate and AMPA has also been demonstrated in other investigations.<sup>4,13</sup> Soil solution sampled by ceramic suction cups installed 15 and 30 cm below the soil surface in two forest soils in northwest Spain, previously treated with glyphosate, was found to have very high peak concentrations of glyphosate: 740  $\mu\text{g L}^{-1}$  at 15 cm and 400  $\mu\text{g L}^{-1}$  at 30 cm.<sup>4</sup> A few high peak concentrations (up to 17  $\mu\text{g L}^{-1}$ ) were also found in leachates from 25 cm long lysimeters with calcareous soil in France.<sup>13</sup> Since both studies were performed with clay-rich soils, they are supposed, although not shown, to have

macropores, and maybe the herbicide transport is colloid facilitated.

### 5.3 Factors affecting glyphosate leaching

While different soil compositions resulting in matrix flow at Jyndevad and preferential flow at Estrup can explain the great difference in glyphosate leachability at these two sites, differences in soil composition can only partly explain the considerably higher leaching at Estrup than at Faardrup, because the soils at both sites have the macropores necessary for preferential flow.<sup>14</sup> However, surplus precipitation at Faardrup was much less (~40%) than at Estrup, and rainfall intensity was low, leaving plenty of time for glyphosate to be sorbed by soil minerals as well as providing limited energy to suspend and transport the particle-bonded glyphosate through the soil. In addition to soil composition and climate, other factors such as timing, tillage and vegetation may possibly also affect glyphosate leaching. The importance of timing is clearly demonstrated by substantial leaching in relation to rainstorms shortly after glyphosate application on structured soils.<sup>4,14</sup> Landry *et al.*<sup>13</sup> found considerably less leaching of glyphosate and AMPA in grass-covered columns than in bare-soil columns filled with calcareous clay soil and installed in a vineyard. In contrast, Fomsgaard *et al.*<sup>100</sup> found no significant difference between glyphosate leaching through low-tillage and normal-tillage soils. In fact, the importance of tillage on glyphosate transport in soils seems unclear according to Vereecken<sup>7</sup>. Finally, although some laboratory column experiments indicate a very limited effect of the phosphate concentration on glyphosate movement,<sup>99</sup> the very strong soil-dependent influence of phosphate on glyphosate sorption and degradation (Sections 3.2 and 4.2) suggests that further investigations, in particular under field conditions, are needed to delineate the role of phosphate on glyphosate leaching in different soils.

In short, on structured soils with preferential flow pathways through macropores, which are mainly found in clayey soils, glyphosate leaching to drains has been demonstrated, but only under special circumstances. Heavy rainfall shortly after glyphosate application seems to be important, while other factors such as vegetation, tillage and phosphate concentration seem to have little or no effect on glyphosate leaching. On the other hand, although leaching to drains indicates a risk of groundwater pollution, the occurrence of glyphosate (and AMPA) in drainage water does not necessarily mean that it will leach to the groundwater except in soils with a very shallow groundwater table. Glyphosate transport by preferential flow in macropores may be considered to be restricted to the upper 1–2 m, since macropore development is closely related to soil formation, which, except in some very old soils, involves less than the top 2 m of parent material.<sup>33,98</sup> Fast and often strong sorption to minerals in



**Figure 7.** Precipitation (A) together with concentrations of glyphosate (B), AMPA (C) and bromide (D) in tile-drainage water (1 m below soil surface) from a Danish structured soil (Glossudalf) with bypass flow in macropores. Grey vertical lines indicate glyphosate application date (13 October 2000). Reprinted from *Journal of Environmental Quality*<sup>14</sup> with permission.

sediment layers between the soil and the groundwater table will remove glyphosate from percolation water (Section 3.2). Furthermore, glyphosate can also be degraded in deep layer sediments.<sup>22</sup> Accordingly, glyphosate is rarely found in groundwaters, as shown by the compilation of Vereecken,<sup>7</sup> and, where found, the concentration is low, although in a few samples it exceeded the European threshold ( $0.1 \mu\text{g L}^{-1}$ ),<sup>27</sup> whereas there seems to be no report of groundwater with concentrations higher than the US MCL ( $700 \mu\text{g L}^{-1}$ ).<sup>26</sup> However, in lowland areas with a shallow groundwater table and low

soil capacity to sorb and degrade glyphosate, use of glyphosate is expected to lead to groundwater pollution.

#### 5.4 Overland-transported glyphosate

In addition to the above-mentioned delivery with drainage water, dissolved and suspended glyphosate can also be transported from terrestrial areas to surface waters by overland runoff. Owing to similar bonding of glyphosate and phosphate in soils, this transport of glyphosate will undoubtedly resemble that of phosphate, which, in turn, is determined by

factors such as rainfall intensity, soil composition, slope characteristics and vegetation that determine water erosion.<sup>60,98</sup> Thus, Siimes *et al.*<sup>18</sup> found that 0.1% of applied glyphosate was lost with surface runoff water within 302 days of application from an uncultivated, bare Finnish field with a slope less than 1%, but they also pointed out the importance of frost-thaw events, and that the observed glyphosate loss is presumably higher than on vegetated fields.

Although comparison with phosphate may aid in identification of risk factors and areas, it is important to be aware of the differences between the two compounds. Soils contain much higher amounts of phosphate (often several orders of magnitude) than of glyphosate. In fact, some cultivated soils are saturated or nearly saturated with phosphate, mainly because of heavy fertilisation over many years.<sup>59–61</sup> It is difficult to imagine that the much lower rates of applied glyphosate will ever saturate soil. Furthermore, in contrast to phosphate, glyphosate is subject to microbial degradation, which reduces the risk of accumulation. Unfortunately, direct knowledge about glyphosate transport by overland flow is very scarce.<sup>18</sup>

Glyphosate running into surface waters because of subsurface leaching through drainage systems or because of overland flow may remain in the aqueous phase or be trapped by sorption in bottom sediments. The extent of surface versus subsurface glyphosate transport is unknown, as is the total glyphosate transfer from land to surface waters, because of lack of research. Further, glyphosate in open waters can also come from other sources such as direct spraying on open waters to control weeds, windborne spray drift from neighbouring sprayed areas and outlets from waste water treatment plants.<sup>3,29</sup> According to recent reports, concentrations of glyphosate (and AMPA) in glyphosate-polluted surface waters can range from sub- $\mu\text{g L}^{-1}$  to  $\text{mg L}^{-1}$  levels.<sup>3,29,30</sup> Whether or not such concentrations can harm sensitive organisms such as amphibians seems, as mentioned in Section 2, an unresolved issue that awaits further research.

## 6 CONCLUSIONS

The review has clearly shown that sorption, degradation and leaching of glyphosate can be very different from soil to soil, and much is still to be learnt about the fate of glyphosate in soils. This variability and uncertainty make it difficult to draw clear and unambiguous conclusions about glyphosate behaviour in soil in general. Nevertheless, it has been shown that glyphosate is sorbed onto variable-charge surface sites, mainly on aluminium and iron oxides and allophane/imogolite, while sorption by permanent-charge layer silicates is limited. Soil organic matter (SOM) seems not to sorb glyphosate, but indirectly SOM may affect glyphosate sorption. Glyphosate is bonded through the phosphonate group to singly coordinated Al–OH and Fe–OH surface sites by strong Al–O–P and Fe–O–P bonds forming mononuclear, monodentate and/or binuclear,

bidentate surface complexes, similarly to sorption of phosphate.

Degradation of glyphosate in soils is mainly a biological process accomplished by different microorganisms, but bacteria, in particular *Pseudomonas*, seem to be the most important. Microbial degradation can occur through the AMPA pathway or through the sarcosine pathway, but, while degradation through AMPA is well documented, the sarcosine pathway is still uncertain. Degradation of glyphosate in soils, which occurs without a lag phase, seems to be a common soil property, but the rate of degradation can be very different from soil to soil.

Similar bonding of glyphosate and phosphate in soils indicates that phosphate may compete with glyphosate on sorption sites, which may affect retention and also degradation of glyphosate. The influence of phosphate on glyphosate sorption and degradation has been suggested repeatedly, but recent investigations show that, while presorption of phosphate can, in some soils (and pure minerals), almost eliminate glyphosate sorption, phosphate has little effect in other soils. Similarly, available phosphate has been found to stimulate glyphosate degradation in some soils, while in other soils it has the opposite or no effect. In order to explain these differences in behaviour, it has been hypothesised that soils possess two kinds of surface site: (i) common sites subject to glyphosate competition and with phosphate preference and (ii) specific sites that are available for either glyphosate or phosphate.

Although sorption and degradation of glyphosate can be very different in different soils, it seems clear that glyphosate leaching is limited in uniform, non-structured soils without macropores, e.g. many sandy soils, and the risk of surface and groundwater pollution with glyphosate (and AMPA) is considered to be low. However, long-term use of glyphosate to control weeds on coarse-textured soil materials such as gravel can lead to glyphosate pollution of groundwater, indicating that sandy, oxide-poor soils may also be at risk, especially in areas with a shallow groundwater table. In structured soils with macropores, i.e. mainly clayey soils, a few studies have indicated that preferential flow may carry glyphosate to drainage systems, but only under special circumstances. Heavy rainfall shortly after glyphosate application seems to be decisive, while other factors such as vegetation, tillage and phosphate concentration seem to have little or no effect. The occurrence of glyphosate in drainage water does not necessarily mean leaching to groundwater, because deeper soil layers may sorb and even degrade the herbicide before it reaches the groundwater, as is also indicated by rarely reported occurrences of glyphosate in groundwater. However, dissolved and suspended glyphosate in drainage water will run into surface waters together with glyphosate transported by surface runoff (presumably resembling overland phosphate runoff), but very little information is available on this transport or on its influence on surface water quality.

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