ADSORPTION OF GLYPHOSATE AND AMPA IN AGRICULTURAL SOILS

ABSORPTION DE GLYPHOSATE ET L'AMPA DANS LES SOLS AGRICOLES

ASSORBIMENTO DI GLIFOSATE ED AMPA IN SUOLI AGRICOLI

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Abstract

Immediately after application glyphosate is mostly adsorbed in the upper 2 cm of soils, and is then transported and adsorbed after few days in deeper soil horizons with concomitant increasing content of its metabolite aminomethylphosphonic acid (AMPA). This work confirmed previous studies, where Fe-oxides seem to play a major role in the adsorption of glyphosate and AMPA in soils: the Chernozem featured lower contents of Fe_d and Fe_o, with consequently lower adsorption of glyphosate and AMPA as compared with the higher weathered Cambisol and Stagnosol.
Keywords: *adsorption, glyphosate, AMPA, soils.*

Résumé

Immédiatement après l'application du glyphosate est surtout adsorbé dans les 2 cm supérieurs des sols, et est ensuite transporté et absorbé après quelques jours horizons profonds du sol avec un contenu croissant concomitante de son métabolite acide aminomethylphosphonic (AMPA). Ce travail confirme les études précédentes, où les oxydes de fer semblent jouer un rôle important dans l'absorption de glyphosate et d'AMPA dans les sols: le tchernoziom vedette des teneurs plus faibles de la Fe_d et Fe_o, avec par conséquent inférieur adsorption de glyphosate et d'AMPA par rapport à la plus altérée Cambisol et Stagnosol.
Mots clés: *absorption, glyphosate, AMPA,sols*

Riassunto

Subito dopo l'applicazione il glifosate viene per lo più adsorbito nei primi 2 cm della parte superiore del suolo, per essere poi trasportato e assorbito nei giorni successivi in orizzonti più profondi del suolo con concomitante aumento del contenuto dell' acido aminomethylphosphonic metabolita (AMPA). Questo lavoro confermando studi precedenti, mostra come gli Fe-ossidi sembrano svolgere un ruolo importante nell'assorbimento del glifosate ed AMPA nei suoli. Il Chernozem evidenzia contenuti più bassi di Fe_d e Fe_o, con conseguente minor assorbimento di glifosa-

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te e AMPA rispetto ai Cambisol e Stagnosol maggiormente interessati da fenomeni di alterazione .

Parole chiave: *adsorbimento,glifosate, AMPA,suoli*

Introduction

Soils play a central role in the regulation of pollutants in ecosystems. Thus, the precise identification and understanding of the processes controlling the behavior of potential environmental contaminants, especially in soils and water, are of major concern.

The behaviour of organic contaminants in soil ecosystems is generally governed by different physical, chemical and biological processes, like sorption–desorption, volatilization, chemical and biological degradation, plant uptake, run-off, and leaching (Mamy *et al.,* 2005).

Among the post-emergency non-selective broad spectrum herbicides, RoundUp Max is applied at a volume of about 60% of the global sales, also in agricultural practice (Candela *et al.,* 2007). Glyphosate (N-(phosphonomethyl)glycine) as the active compound in RoundUp Max is an acid, but it is commonly used as a salt, most commonly as isopropylammonium salt and is a polar, highly water-soluble substance that easily forms complexes with metals and binds tightly to soil components (Gimsing *et al.,* 2004, Schnurer *et al.,* 2006, Ghanem *et al.,* 2007).

The persistence of glyphosate is typically up to 170 days, with a half-life time of 45-60 days, (Peruzzo *et al.,* 2008). . The major degradation product of glyphosate is aminomethylphosphonic acid (AMPA), (Peruzzo *et al.,* 2008, Locke and Zablotowicz, 2004, Gimsing *et al.,* 2004).

Depending on soil composition but also on the specific geomorphological local conditions (Locke and Zablotowicz, 2004, Soulas and Lagacherie, 2001, Gimsing *et al.,* 2004), traces of this herbicide were found in many surface- and groundwater systems, (Landry *et al.,* 2005, Peruzzo *et al.,* 2008). Consequently, the use of this herbicide should be much more related to the characteristics of the application site, (Soulas and Lagacherie, 2001).

The aim of this study was to investigate the behavior of glyphosate and AMPA at different soils and time intervals after field application.

Material and methods

Three soils under different climatic conditions and with distinguished physico-mineral composition were investigated:

a sandy stagnic Cambisol (WRB, 2006) at Kirchberg (Styria) from tertiary carbonate free sediments, a loamy Stagnosol (WRB, 2006) from carbonate free sediments (flysch, sandstone) at Pyhra (Lower Austria) and a Chernozem (WRB, 2006) from loess at Pixendorf (Lower Austria). Based on their contrasting physico-chemico-mineralogical parameters e.g. texture, carbonate content, pH-value, and Fe-oxides these soils were selected for a better understanding on the glyphosate behavior and extraction from soils

The soils investigated are representative for the main agricultural regions of Austria, were Cambisols cover approx. 50%, Chernozems approx. 18% and Stagnosols approx. 10% of the agricultural land use of Austria, (Haslmayr, 2010).
The herbicide application was performed at all three sites according to the common agricultural practice, i.e. 4 liters Roundup Max (450 g glyphosate /L Roundup Max) dissolved in 200 liters of water and applied per ha (2 % herbicide solution). This corresponds to an application of 1800 g glyphosate ha^{-1} or 180 mg glyphosate m^{-2}.
In order to investigate the fate of glyphosate and AMPA in depth and time after Roundup Max application, soil bulk samples were taken at different time intervals after application at 10 points within each field replication (pooled than to one sample per site) as follows:

Kirchberg :
a) immediately after the Roundup Max application, at 0-2 cm soil depth;
b) 3 days after application at 0-2 cm and 2-5 cm soil depth;
c) 12 days after application at 0-2 cm, 2-5 cm and 5-10 cm soil depth;

Pyhra:
a) immediately after the Roundup Max application, at 0-2 cm soil depth;
b) 28 days after application at 0-2 cm, 2-5 cm and 5-10 cm soil depth;

Pixendorf:
a) immediately after the Roundup Max application, at 0-2 cm soil depth;
b) 3 days after application at 0-2 cm and 2-5 cm soil depth;
c) 10 days after application at 0-2 cm, 2-5 cm and 5-10 cm soil depth;

Results and discussion

The silty Chernozem is slightly alkaline with a medium carbonate content. The siliceous Stagnosol and Cambisol are weakly acidic, according to their formation conditions. The contents of soil organic matter decrease with soil depth (Table 1).
Pedogenic Fe-(Al)-oxides play a major role as absorbers for glyphosate in soils. The dithionite-soluble Fe (Fe_d) indicates the total amount of pedogenic formed Fe-oxides. This Fe-extraction does not allow any conclusion about the type of Fe-oxide (goethite is however the most relevant Fe-oxide in Central Europe).
The Chernozem features a low content, the Stagnosol a medium content and the Cambisol a high content of Fe-oxides (Table 2). Consequently, the expected sorption capacity for glyphosate and AMPA increases respectively from the Chernozem, over the Stagnosol to the higher weathered Cambisol.
Many results from the literature show that Fe-oxides play an important role in the soil adsorption of glyphosate. From the investigated Fe-oxides (ferrihydrite, hematite and goethite) ferrihydrite had the highest impact on the adsorption process of glyphosate (Mentler *et al.,* 2007).The variation of the KD-values in different soils is significant (Mentler *et al.,* 2007) and seems to depend mainly on the Fe-oxide content (Table 3).

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Table 1. *General chemical parameters of the investigated soils*

Site	Pixendorf		Kirchberg		Phyra	
Soil type (WRB)	Chernozem		Cambisol		Stagnosol	
Depth (cm)	0-5	5-20	0-5	5-20	0-5	5-20
Nt (%)	0.13	0.11	0.13	0.11	0.12	0.10
Ct (%)	3.7	3.1	1.7	1.5	1.6	1.2
$CaCO_3$ (%)	14.7	15.4	<0.5	<0.5	<0.5	<0.5
C_{anorg} (%)	1.80	1.85	0.0	0.0	0.0	0.0
C_{org} (%)	1.86	1.25	1.73	1.51	1.61	1.17
OM (%)	3.2	2.2	3.0	2.6	2.8	2.0
pH ($CaCl_2$)	7.3	7.3	5.7	5.8	5.7	5.6
C/N	14.8	11.4	13.3	13.7	13.4	12.2

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Table 2. *Fe-oxide distribution (mg.kg^{-1} soil) in the investigated soil*

Site	Pixendorf		Kirchberg		Phyra	
Soil type (WRB)	Chernozem		Cambisol		Stagnosol	
Depth (cm)	0-5	5-20	0-5	5-20	0-5	5-20
Fe_p* (mg.kg^{-1})	37	39	530	569	550	538
Fe_o** (mg.kg^{-1})	983	1040	3422	3726	3241	3215
Fe_d*** (mg.kg^{-1})	7970	8378	14843	15032	9959	9918
Fe_o/Fe_d	0.12	0.12	0.23	0.25	0.32	0.32

Fe_p* = organic bound Fe-oxides, pyrophosphate-soluble
Fe_o** = „amorphous“ (weakly crystallized) Fe-oxides, oxalate-soluble
Fe_d*** = well crystallized Fe-oxides, dithionite-soluble

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Table 3. *Soil properties and KD-values for glyphosate for different soils and silica sand based on literature data (after Mentler et al., 2007)*

	KD-value [l/kg]	pH-value	Clay [mass%]	Corg [Mass.%]	Fe [Mass.%]	Location
Mentler *et al.*, 2007	467 - 519	4.5	2.7	0.8	3.2	Wienerwald
Mentler *et al.*, 2007	13.8 – 29.3	5.8	17.2	3.45	2.2	Phyra
Mentler *et al.*, 2007	188 - 299	5.2	18.8	6.7	2.1	Eurosoil 7
Mentler *et al.*, 2007	1.5 – 2.9	6.4	<0.1	<0.01	< 0.01	Silica sand
Sorensen *et al.*, 2006	271 - 385	4.3-5.6	2-4	0.1-4.9	0.01-0.05	Fladerne Beak
Mamy *et al.*, 2005	13.2 - 31.1	8.2-8.5	8.8-9.5	1.3-2	0.16-0.19	Chalons

The results of the glyphosate and AMPA investigations:
Chernozem (Fig. 1-2):
At the first sampling after field application of Roundup Max about 30% of the applied glyphosate amount could be detected in the upper 0-2 cm of the soil. The main part of the herbicide adheres at the green plant cover and at first does not

enter the soil surface. After 3 days the glyphosate content decreased in the topsoil and was transported and adsorbed in the deeper horizon (2-5 cm) with concomitant increase of the AMPA content.

Figure 1. *Chernozem: glyphosate contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 3 days after application; 3. sampling = 10 days after application; control = residues before application).*

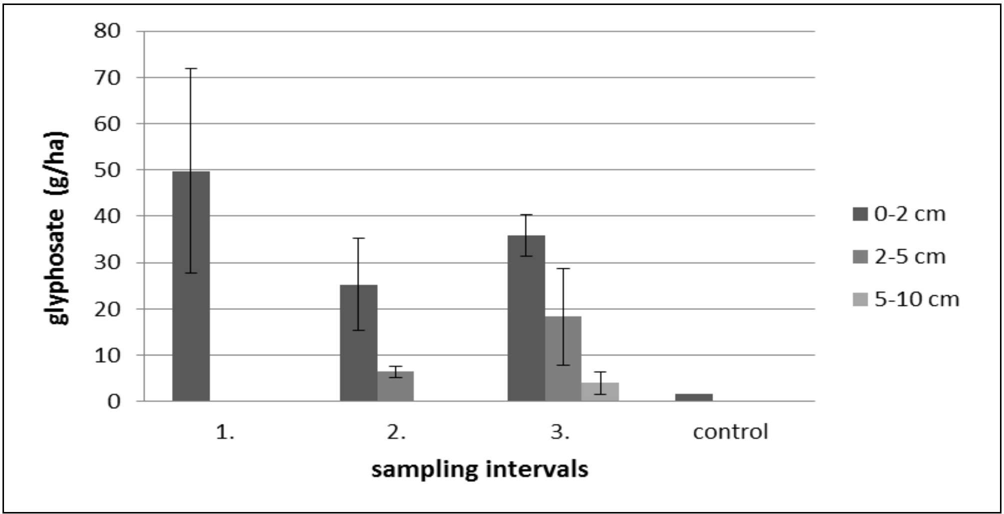
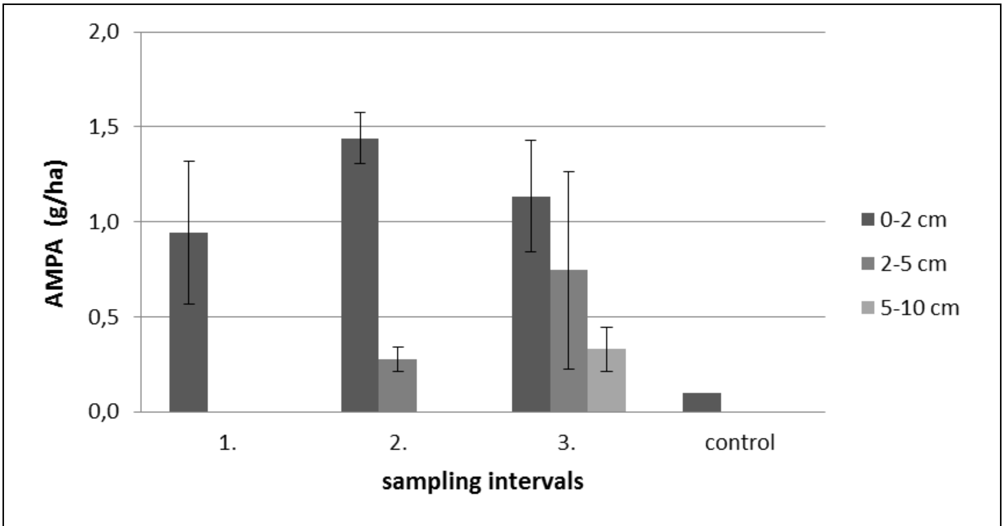


Figure 2. *Chernozem: AMPA contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 3 days after application; 3. sampling = 10 days after application; control = residues before application).*



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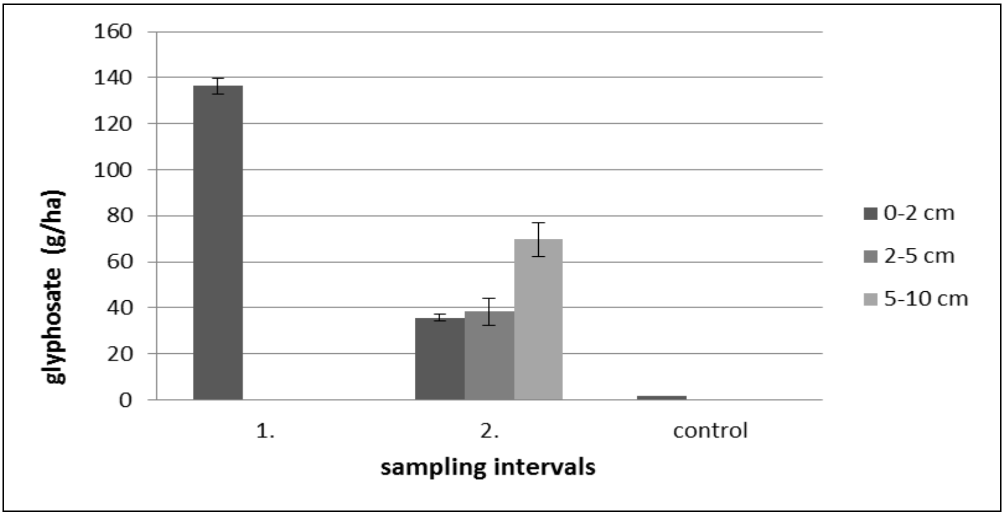
After 10 days the glyphosate content was even higher than immediately after application, which can be explained by: a) plant-adsorbed glyphosate is released to the topsoil after partly decomposition of the weeds; b) during the time between second and third soil sampling about 10 mm precipitation fell down, this may have washed glyphosate from plant leaves out. The increase of AMPA 3 days after application of Roundup Max shows the very quick degradation of glyphosate to AMPA. This degradation could probably take place already in the Roundup Max package, this would explain the fact that AMPA was detected immediately after the Roundup Max application.

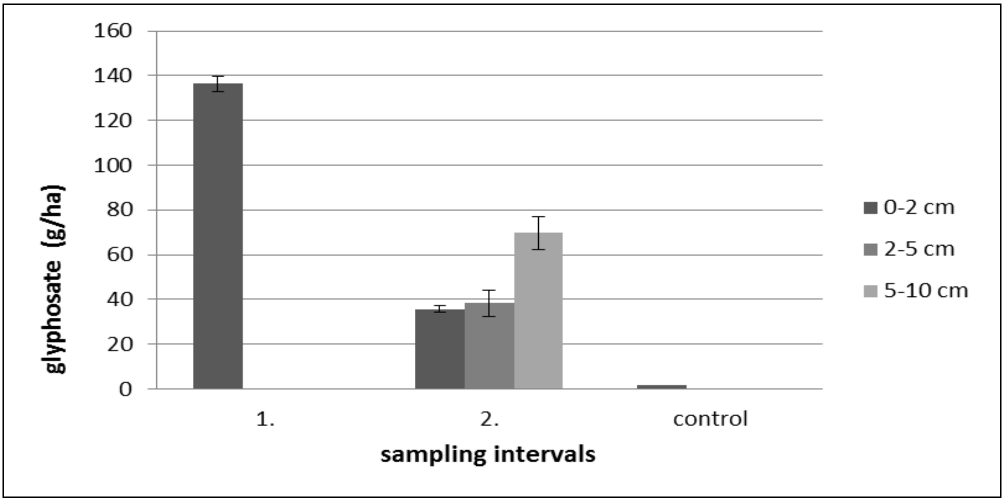
Stagnosol (Fig. 3-4):
Most of the applied glyphosate was transported and adsorbed in deeper horizons after 28 days. The reference (control) glyphosate and AMPA values in Fig. 3 and 4 refer the amount of both substances before application, residuals of previous applications (2 years before). That means that in the Stagnosol glyphosate is transported downwards within 2 years and probably bound to deeper soil layers.

Figure 3. *Stagnosol: glyphosate contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 28 days after application; control = residues before application).*



Cambisol (Fig. 5-6).
The Cambisol has the best potential adsorption capacity for glyphosate with about 16.000 mg $Fe_d.kg^{-1}$ soil and about 3.500 mg $Fe_o.kg^{-1}$ soil (Table 2), but previous studies with rain simulation experiments (Rampazzo Todorovic *et al.*, 2010) showed how that site can be strongly influenced by erosion processes if the infiltration rate for rainfall is reduced by soil crusting.

Figure 4. *Stagnosol: AMPA contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 28 days after application; control = residues before application).*



This is the reason why glyphosate strongly decrease in the upper soil horizons but does not accumulate in deeper horizon. A considerable amount of the applied glyphosate may be transported downslope with runoff (Rampazzo Todorovic *et al.*, 2010). Moreover, the degradation from glyphosate to its metabolite AMPA is visible by the increase of AMPA with time.

Figure 5. *Cambisol: glyphosate contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 3 days after application; 3. sampling = 12 days after application; control = residues before application).*

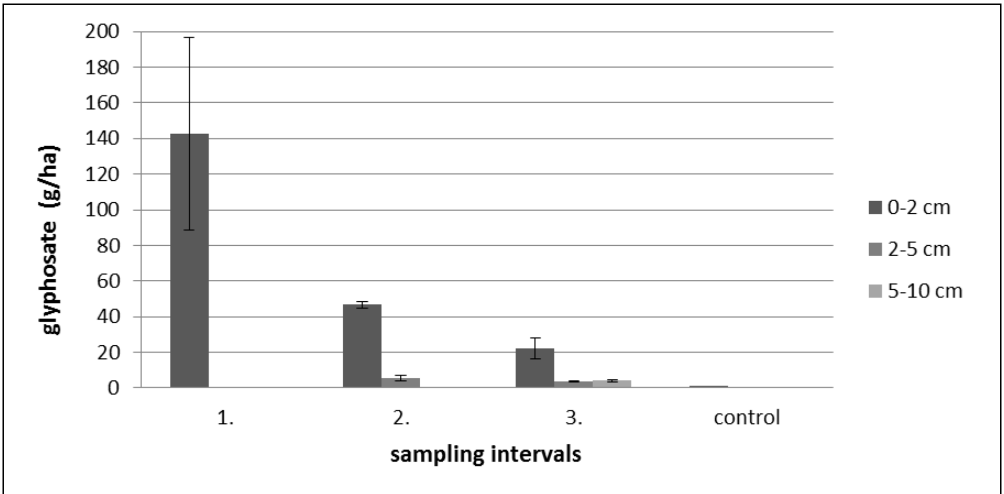


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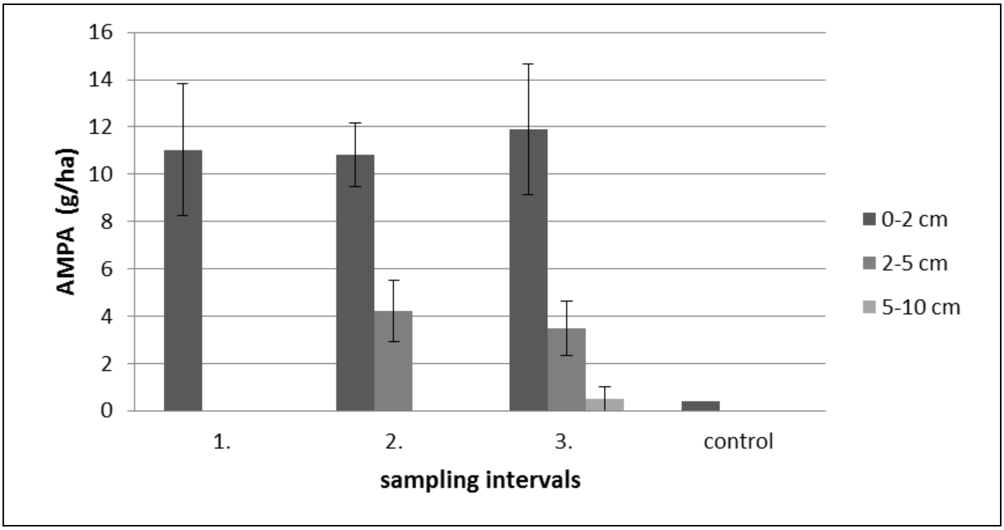
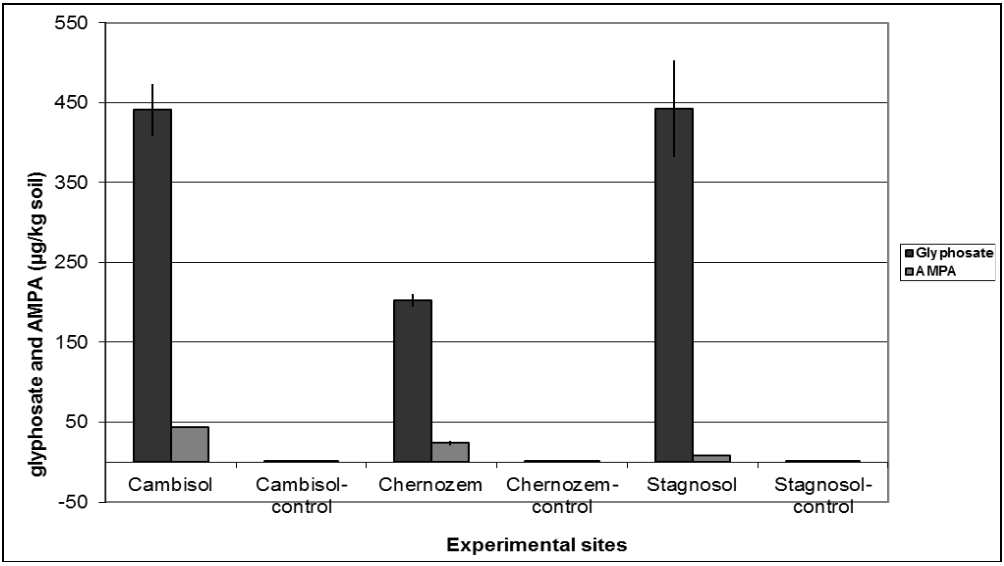
Figure 6. *Cambisol: AMPA contents in soil at different time intervals and soil depths. (1. sampling = immediately after application; 2. sampling = 3 days after application; 3. sampling = 12 days after application; control = residues before application).*



The results presented in Fig.7 show distinguished contents of glyphosate and AMPA in the 3 investigated soils according to their chemical-mineralogical adsorption properties.

Figure 7. *Glyphosate and AMPA contents in the investigated soils at 0-2 cm soil depth. The control values show the glyphosate contents before application (e.g. the residual traces, next to zero, from the previous application).*



Based on previous studies, we expected that glyphosate and AMPA would be more strongly adsorbed in soils with a higher Fe-oxide (Fe_d) content (Mentler *et al.*, 2007; Pessagno *et al.*, 2008). Our results show this trend, where both the Cambisol and the Stagnosol, with a higher pedogenic Fe-oxide content, 15000 and 10000 mg Fe_d kg^{-1} soil, respectively, (Table 2), adsorbed a distinctly higher quantity of glyphosate and AMPA than the Chernozem which had a distinctly lower Fe-oxide content, (7900 mg Fe_d kg^{-1} soil, see Table 2), and a Kd-value about 10 times lower than the Cambisol (Klik *et al.*, 2010).
Moreover, the weakly weathered Chernozem consequently shows a low content of amorphous (Fe_o) Fe-oxides (973 mg Fe_o kg^{-1} soil) with respect to the more highly weathered Cambisol (3402 mg Fe_o kg^{-1} soil) and Stagnosol (3279 mg Fe_o kg^{-1} soil), see Table 2. Higher content of pedogenic Fe-oxides (Fe_d) (Barja *et al.*, 2001; Zhou *et al.*, 2004; Gimsing *et al.*, 2004; Morillo *et al.*, 2000) and even higher contents of amorphous Fe-oxides (Fe_o) lead to higher sorption of glyphosate and AMPA, probably due to a larger and more reactive surface area of amorphous Fe-oxides. Thus, Fe-oxides in general seem to be a key parameter for glyphosate and AMPA adsorption in soils. Our study confirmed this: the analysis showed lower contents of Fe_d and Fe_o for the Chernozem, with consequently lower adsorption of glyphosate and AMPA compared with the Cambisol and the Stagnosol.

Conclusions

Shortly after Roundup Max application only a part of the applied glyphosate amount enter the upper 0-2 cm of the topsoil and is then transported and adsorbed in deeper horizons with time with concomitant increase of the AMPA content.
The results showed distinguished contents of glyphosate and AMPA in different soils at the same soil depth, according to their chemical-mineralogical adsorption properties, especially Fe-oxides (Fe_d and Fe_o).
Thus, iron-oxides in general seem to be a key parameter for glyphosate and AMPA adsorption in soils.

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