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BEHAVIOR OF ORGANIC POLLUTANTS IN THE SOIL ENVIRONMENT. SPECIAL FOCUS ON GLYPHOSATE AND AMPA

COMPORTEMENT DES AGENTS POLLUANTS ORGANIQUES DANS LE SOL. AVEC MENTION SUR LE GLYPHOSATE ET AMPA

BEHAVIOR OF ORGANIC COMPORTAMENTO DEGLI INQUINANTI ORGANICI NELL'AMBIENTE DEL SUOLO. FOCUS SPECIALE SU GLYPHOSATE E AMPA

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Abstract

In industrialized countries, soil and groundwater contamination by various forms of harmful substances is a contemporary problem in this highly industrialized age. In this document, the state of the art regarding the main mechanisms, processes and factors governing the fate and behavior of organic contaminants in the soil-ground water system is reviewed. The behavior of organic contaminants in soils is generally governed by a variety of complex dynamic physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching. These processes directly control the transport of contaminants within the soil and their transfer from the soil to water, air or food. The relative importance of these processes varies with the chemical nature of the contaminant and the properties of the soil. Both the direction and rate of these processes depend on the chemical nature of the organic contaminant and the chemical, biological, and hydraulic properties of the soil. Some organic contaminants are degraded in the soil within a certain time. On the other hand some are degraded only slowly or are sequestered within soil particles thus being inaccessible for microbial degradation. Persistence in soils increases the potential for environmental consequences. Mobility in soil environments is a key factor in assessing the environmental risk. Compounds interacting weakly or not at all with soil surfaces will be leached together with the soil solution and have the potential for contaminating surface or ground water reservoirs far from the point of getting into the soil. Clays, oxides and organic matter are the primary constituents in soils responsible for the sorption of organic contaminants. Among the organic contaminants used in agriculture, one of the most world-wide applied herbicides is glyphosate, an organophosphonate product, with broad spectrum of application. Results of two field experiments conducted in two sites of Austria show the influence of different tillage systems, vegetation cover, and site specific properties on the risk of surface run off of glyphosate. Better understanding of the behavior of glyphosate is needed (e.g. adsorption conditions, environmental influence, specific soil parameters, soil microbes behavior) for a better risk assessment of

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environmental pollution., degradation rates and consequently risks of contamination for surface and groundwater involved can be estimated.

Keywords: organic contaminants; risk of environmental contamination; glyphosate; surface run off; adsorption; soil properties; soil processes.

Résumé

Dans les pays industrialisés, la contamination du sol et des eaux causée par les différentes formes des substances dangereuses est un problème très actuel dans notre époque. Ce document présente l'état de l'art des principaux mécanismes, processus et facteurs dont dépendent l'évolution et le comportement des polluants organiques dans le système du sol et des eaux phréatiques. En ligne générale, le comportement des polluants organiques dans les sols est réglé par l'ensemble à la fois complexe et dynamique des processus physiques, chimiques et biologiques, y compris l'adsorption et la désorption, la volatilité, la dégradation chimiques et biologiques, l'absorption des plantes, le ruissellement de surface et le lessivage produit par l'eau. Ces processus contrôlent directement le transfert des contaminants dans les sols et du sol aux eaux, à l'air et à la nourriture. L'importance relative de ces processus varie en fonction de la nature chimique des polluants et des propriétés des sols. Les deux, c.-à-d. la direction et l'ampleur de ces processus, dépendent de la nature chimique des polluants chimiques et des propriétés chimiques, biologiques et hydrauliques des sols. Certains polluants chimiques se dégradent dans les sols en un certain laps de temps. D'autres ne se dégradent que très lentement ou bien ils restent séquestrès pris dans des particules de sols en devenant de ce fait inaccessibles à la dégradation microbiologique. Leur persistance dans les sols augmente les conséquences potentielles sur l'environnement. La mobilité dans le sol est le facteur principal pour l'évaluation du risque environnemental. Des composants qui ne réagissent que faiblement ou qui ne réagissent pas du tout avec les surfaces du sol sont emportés avec la solution du sol par l'érosion due aux eaux et ils peuvent polluer les nappes même loin de leur point d'entrée dans le sol. Les argiles, les oxydes de métaux et la matière organique sont les principaux composants du sol responsables de l'adsorption des polluants organiques. Parmi les polluants organiques utilisés en agriculture, un des herbicides les plus largement utilisés est le glyphosate, un produit organophosphatique au large spectre d'activité. Les résultats de deux expériences effectuées en deux localités différentes en Autriche prouvent l'influence des différents modes de culture du sol, de la couverture végétale du sol et des propriétés spécifiques des différentes localités sur le risque de ruissellement superficiel du glyphosate. Une meilleure compréhension du comportement du glyphosate (par exemple, les conditions de l'adsorption, l'influence de l'environnement, les paramètres spécifiques des sols, le comportement des microbes du sol) s'impose pour pouvoir mieux évaluer le risque de pollution de l'environnement. Suite à ce type d'analyse, il est possible d'évaluer l'adsorption, la proportion de dégradation et les risques dus à la pollution des eaux de surface et des nappes.

Mots clés: polluants organiques; risque de pollution environnementale; glyphosate; ruissellement de surface; adsorption; propriétés du sol; processus dans le sol.

Riassunto

Nei paesi industrializzati, la contaminazione del suolo e l’acqua causata dalle diverse forme delle sostanze pericolose, è un problema molto attuale in questa era industrializzata. In questo documento, è presentato lo stato dell’arte dei meccanismi principali, processi e fattori, i quali governano il fato e il comportamento degli inquinanti organici nel sistema del suolo e le acque freatiche.
Il comportamento degli inquinanti organici nei suoli, è regolato in generale dalla varietà dei complessi e dinamici processi fisici, chimici e biologici, compreso assorbimento -desorbimento, volatilità, degradazione chimica e biologica, assorbimento dalle piante, run-off e dilavamento. Questi processi controllano direttamente il trasporto dei contaminanti nei suoli e il loro trasferimento dai suoli nelle acque, l’aria e il cibo. L’importanza relativa di questi processi varia con la natura chimica degli inquinanti e le proprietà dei suoli. Entrambi, la direzione e la dimensione di questi processi, dipendono della natura chimica degli inquinanti chimici e le proprietà chimiche, biologiche e idrauliche dei suoli. Alcuni inquinanti organici sono degradati nei suoli entro determinato tempo. Dall’altra parte, alcuni possono essere degradati solamente molto lentamente oppure sono sequestrati dentro le particole del suolo, e in tale modo diventano inaccessibili per la degradazione microbiologica. La persistenza nei suoli fa aumentare la potenzialità delle conseguenze circostanti. Mobilità nel suolo è il fattore principale per valutazione del rischio ambientale. Componenti che reagiscono debole oppure non reagiscono con la superficie del suolo, saranno dilavate con la soluzione del suolo e potenzialmente potrebbero inquinare le acque falde anche lontano dalla entrata nel suolo. Le argille, ossidi dei metalli e la sostanza organica, sono le componenti principali nel suolo per assorbire gli inquinamenti organici. Tra gli inquinanti organici usati nell’agricoltura, uno degli erbicidi più usati nel mondo, è glyphosate, il prodotto organofosfatico, con il largo spettro delle applicazioni. Risultati dei due sperimenti condotti nelle due località diverse nell’Austria, dimostrano l’influenza delle diverse coltivazioni del suolo, la copertura vegetale del suolo e le proprietà specifiche delle località diverse sul rischio del run-off superficiale del glyphosate.
La comprensione migliore del comportamento del glyphosate è necessaria (per esempio, le condizioni dell’assorbimento, influenza ambientale, i parametri specifici dei suoli, il comportamento dei microbi del suolo) per la valutazione migliore del rischio per l’inquinamento dell’ambiente. Basato su questa comprensione, la valutazione dell’assorbimento, proporzione della degradazione ed i rischi conseguenti dell’inquinamento delle acque superficiale e falde è possibile.

Parole chiave: inquinanti organici; rischio dell’inquinamento ambientale; glyphosate; run-off superficiale; assorbimento; proprietá del suolo; processi nel suolo.

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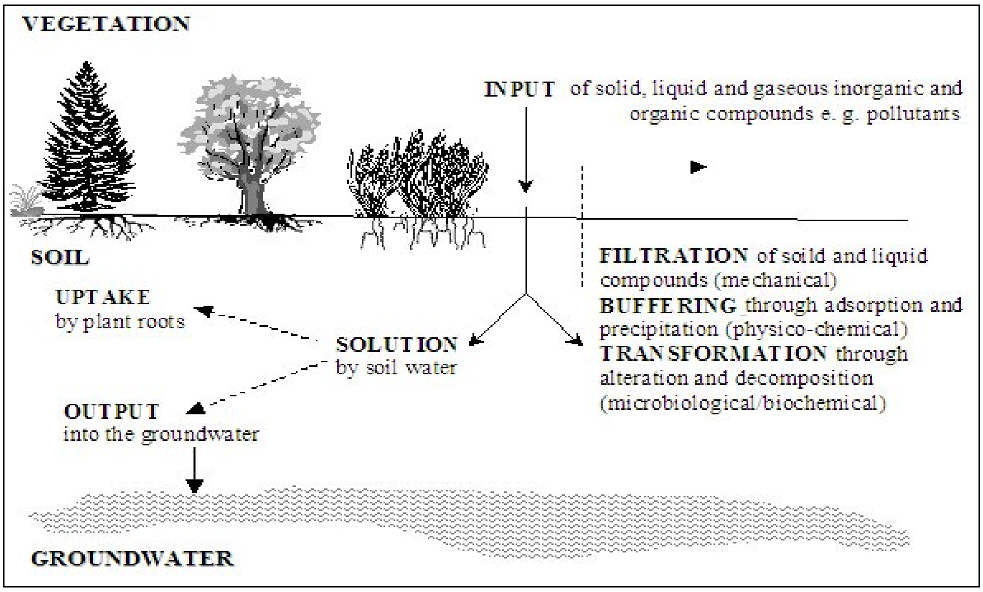
Introduction

Organic pollutants are mainly man-made and industrially produced. Nowadays they are present in water systems, run-off, soil and food (Ternan *et al.*, 1998). Soils play an important role in the regulation of contaminants in ecosystems. There is a growing concern about identifying and understanding the mechanisms controlling the fate of chemicals which are threat for non-target organisms and a source of environmental contamination, especially of water sources. Since the organic pollutants are released in environment often in enormous quantities and among the herbicides the most applied is glyphosate, there is a considerable risk of these pollutants. A better understanding of organic behavior in soils is important for the improvement of environmental protection. There is a need for more specified pesticide management based on the adaptation of the pesticide type and application rates to the characteristics of the area of application (Eriksson *et al.*, 2007; Crommentuijn *et al.*, 2000; Zablotowicz *et al.*, 2006; Lupwayi et al., 2007; Peruzzo *et al.*, 2008; Renaud *et al.*, 2004; Warnemuende *et al.*, 2007; Albrechsten *et al.*, 2001; Papiernik SK, 2001).

The behaviour of organic contaminants in soils is generally governed by a variety of physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching (Fig.1) (Mamy *et al.*, 2005).

Figure 1 - *Role of the soil in the fate of contaminants in the environment.*



Special focus of this presentation is given on glyphosate and AMPA. Glyphosate is an organophosphonate herbicide, nowadays one of the most applied in the world with increasing importance.

Glyphosate fate and behavior in soil is affected by different soil factors and processes, but depends also on interaction between herbicide and soil under the specific local conditions (Locke & Zablotowicz, 2004; Soulas & Lagacherie, 2001; Gimsing *et al.*, 2004).

Knowledge of glyphosates behavior depends on our understanding of herbicide characteristics, environmental influence, specific soil parameters and soil microbes behavior. Based on this knowledge, time dependent adsorption/degradation rates and consequently risks for environmental pollution involved can be estimated and better attenuated.

Dissipation ways of the organic pollutants

Dissipation of organic contaminants in soils is generally governed by different physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching (Fig. 2). Sorption by soil solids is characterized by a number of mechanisms like hydrophobic interaction, water solubility, ligand exchange, charge transfer, hydrogen bonding, ion exchange (Pitter & Chudoba, 1990, Schwarzbauer 2005).

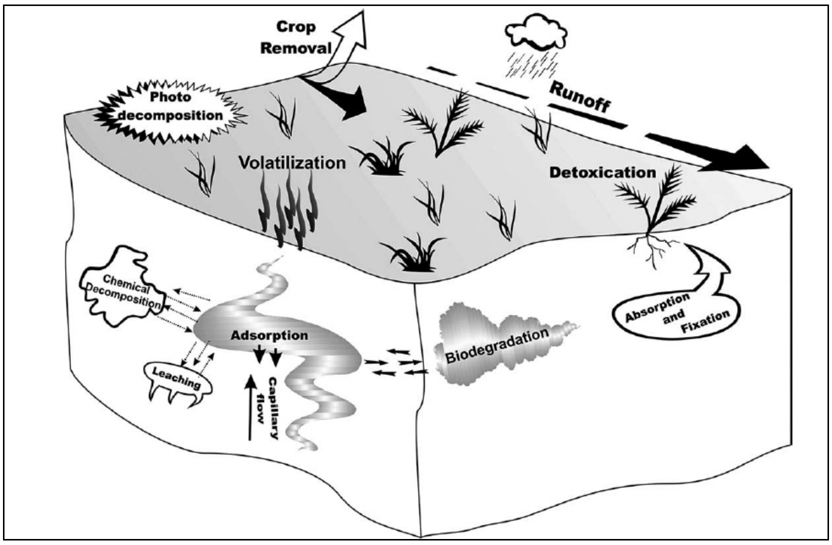


Figure 2

Dissipation ways of organic pollutants in soil (Andreu & Pico, 2004).

The distribution (horizontally and vertically) of organic pollutants in soils depends on their movement and degradation. Movement and degradation of organic pollutants in turn depend on three general factors:

- Properties of the pollutant
- Chemical, biological and hydraulic properties of the soil
- Weather conditions

Movement of the organic pollutants can be due to diffusion and mass flow.

On the other hand, dissipation ways of contaminants are also time dependent (e.g. different biodegradation phases; leaching and surface runoff-risk) (Nicholls, 1991, Schwarzbauer, 2005).

The attenuation of pollutant toxic concentration in soils is governed by processes of precipitation, sorption and immobilization. Due to these processes particular soil components can diminish the risk of water, air and food contamination with organic pollutants.

Glyphosate

Glyphosate is a post-emergency non-selective broad spectrum herbicide which blocks the shikimic acid pathway for biosynthesis of aromatic amino acids in plants, also in some microbes, but not in all soil microorganisms (Haghani K *et al.*, 2007).

This herbicide is worldwide used in agriculture, railways, dam protection, surface water systems, urban areas (Nowack, 2002; Ternan *et al.*, 1998; Baylis, 2000).

Usually the persistence is up to 170 with usual half life of 45-60 days (Peruzzo *et al.*, 2008), but there is also investigations which showed that half-life could be prolonged up to years (Carlisle and Trevors, 1978 in Zaranyika and Nyandoro, 1993; Eberbach, 1997). Its main metabolite is AMPA (Peruzzo *et al.*, 2008; Locke & Zablotowicz, 2004; Gimsing *et al.*, 2004).

Soil parameters governing the glyphosate fate in environment. Generally, the following factors could be stated as crucial (Locke & Zablotowicz, 2004; Soulas & Lagacherie, 2001; Gimsing *et al.*, 2004):

- *total inner surface* of the soil (total surface of the pore system / pore walls); this surface is mostly electrically charged and therefore of main importance for adsorption processes. To give a practical example how large this surface can be, if one assumes 1ha of soil at a depth of 20 cm, an average bulk density of 1.5 Mg/m3, a clay content of 20% and a content on OM of 3%, which are rather average values for soils, it sums up at a total surface of 210.000 km2. Now it can be concluded that for example the total surface of Germany (about 367.000 km2) is contained in 1.7 ha of soil and 20 cm depth.
- *constituents of the inner soil surface* (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative);
- *environmental influence;*
- *specific soil parameters;*
- *soil microbes behavior;*
- *P availability.*

Estimation of time dependent degradation rates and consequently risks involved is very important (e.g. glyphosate biodegradation at the beginning is generally fast, then slower- with enhanced adsorption processes; Glyphosate leaching and surface runoff-risk is bigger with the rain immediately after the application, before the plants could adsorb it) (Eriksson *et al.*, 2007; Peruzzo *et al.*, 2008; Zaranyika and Nyandro, 1993; Siimes et al., 2006).

Glyphosate sorption in soil. Strong sorption of glyphosate to soil particles may decrease degradation rate of glyphosate due to less bioavailability of bounded pesticide.

- Glyphosate adsorption on soil colloids;
- Fe/Al-oxides, clays, calcite, organic matter (?);
- Glyphosate complexation with metals.

Availability of glyphosate for decomposition is affected by the rate of desorption. (Eberbach, 1997; Gimsing *et al.*, 2004; Schnurer *et al.*, 2006; Sørensen et al., 2006; Rodrígez-Cruz et al., 2006; Kools *et al.*, 2005; Ghanem *et al.*, 2007)

Table 1: Soil properties and the 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 [w/w%]**	**Corg [w/w.%]**	**Fe [w/w.%]**	**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
Dousset et al., 2004	8.5 - 10231	-	-	-	-	Burgundy
Mamy et al., 2005	13.2 - 31.1	8.2-8.5	8.8-9.5	1.3-2	0.16-0.19	Chalons

Glyphosate fate is affected by the soil processes and their influence on soil microbial population and activity. Numerous investigations have shown that the next factors have great influence on pollutant fate in different soils (Mamy *et al.*, 2005; Albrechsten *et al.*, 2001; Eberbach, 1997; Blume *et al*., 2002; Kools *et al.*, 2005; Stenrød M *et al*., 2005; Stenrød M *et al*., 2007; Matthies *et al.*, 2008; Fenner *et al*., 2005):

- Temperature
- Moisture
- pH
- Aerobic/anaerobic conditions (redox conditions).

Sorption of glyphosate in soil is mainly due to the inner sphere complex formation with metals of soil oxides, related to the soil phosphate adsorption capacity.
Possible binding mechanisms:

- Electrostatic bonds in extremely acid media

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- Hydrogen bonds with humic substances
- Especially, covalent bonds with Fe and Al oxides.

Glyphosate sorption on iron oxides. The results in the literature show that iron oxides play an important role in the soil retention of glyphosate. From the investigated iron 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 iron oxide content. A low sorption capacity could result in leaching to the groundwater.

Biodegradation of glyphosate. Microbial populations are responsible for the vast majority of biotic transformations in the environment. There is ongoing debate about the main biotransformation type of glyphosate in soil:

- Co-metabolic biodegradation
- Proliferation (growth-linked) biodegradation

In numerous studies glyphosate degradation was observed as co-metabolic process. (Krzysko-Lupicka and Sudol, 2008; Gimsing *et al.*, 2004)
In some other studies microorganism biodegradation of organophosphonates (glyphosate) was proliferation type (Krzysko-Lupicka *et al.,* 1997; Obojska *et al.,* 1999, Dick and Quinn 1995).

Till now, different soil microbes were detected as a biotransformator of glyphosate (Tykva, 1998; Gimsing *et al.,* 2004; Foster *et al.,* 2004; Balthazor and Hallas, 1985; Singh *et al.,* 2005; Arbeli and Fuentes, 2007; Dyhrman *et al.,* 2006; Liu *et al.,* 1991; Hayes et al., 2000; McMullan G *et al.,* 1993; Pipke and Amrhein 1988; Kishore and Jacob, 1987; Jacob GS *et al.,* 1988; Lipok et al., 2007; Krzysko-Lupicka *et al.,* 1997; Krzysko-Lupicka and Sudol, 2008; Obojska *et al.,* 1999; Forlani G *et al.,* 1999; Obojska *et al.,* 2002; Dick and Quinn 1995; Vathanomsat and Brown, 2007):

- Bacterial strains - (*Pseudomonas* sp., Agrobacter, *Arthrobacter* sp., *Rhizobium meliloti*, Streptomycin, *Escherichia coli*, *Flavobacterium* sp. etc.)
- Fungi – Fusarium (Phytopathogenic, potentially dangerous in soil environment (Krzysko-Lupicka and Sudol, 2007)), Trichoderma harzianum, *Scopulariopsis* sp., *Aspergilus niger, Geobacillus caldoxylosilyticus* etc.
- Yeasts – (Metal complexes affinity?)
- Marine diazotroph *Trichodesmium*
- Cyanobacetria *Spirulina* spp.
- Actynomycete *Streptomycete* isolates
- Unculturable soil microorganisms

Glyphosate biodegradation pathways. The pathways and rates of microbial degradation in the environment will depend on a wide range of factors regulating microbial population, size and ability to metabolize (Warren *et al.,* 2003). Two major mechanisms have been described for the utilization of phosphonates by microorganisms:

- AMPA pathway due to C-N cleavage by oxidoreductase flavoprotein;
- Sorcosine pathway due to C-P cleavage, the product of degradation is glycine.

(Gimsing *et al.,* 2004; Warren *et al.,* 2003; Dyhrman *et al.,* 2006; Hayes et al., 2000; Liu *et al.,* 1991; Rueppel ML *et al.,* 1977; Lipok et al., 2007; Krzysko-Lupicka and Sudol, 2008; Krzysko-Lupicka *et al.,* 1997; Obojska *et al.,* 1999; Forlani G *et al.,* 1999; Obojska *et al.,* 2002; Dick and Quinn 1995)

Environmental fate of metabolites

There is still a lack of data for better understanding of environmental fate of AMPA (Peruzzo *et al.*, 2008). Till know we know that AMPA is slow degraded as glyphosate, but there is not enough data about AMPA accumulation. There are still questions to be answered e.g. Should be AMPA considered as POP? What about other glyphosate metabolites?

Surface run-off. In some previous study the lack of runoff for glyphosate was observed, probable due to the tight bonding to the soil (Rueppel ML *et al.,* 1977). Since glyphosate is water soluble there is a potential risk of run-off in the case of erosive precipitations very soon after the herbicide application and in the regions with high risk of run-off.
Field experiments conducted in Kirchberg after corn yield (Stiria/Austria) on cambisol and Pixendorf after cereal yield on chernozem (Lower Austria/Austria) in September 2008 using a rainfall simulator under worst case scenario (e.g. 50 mm rain in 1 hours immediately after glyphosate application) showed following results:

- Glyphosate is not equally retained by the soil and can be dispersed with run off up to 45% of the applied amounts.
- No tillage plots show a much higher concentration of glyphosate in run-off than conventional tillage. However, the total sum of glyphosate in run off was higher on conventional tillage on Pixendorf site where the high infiltration capacity of the no tillage plots prevented the run off. On the Kirchberg site the crusted soil surface caused the high run off as well as corn crop cover.
- For drawing final conclusions about the risk of glyphosate dissipation through erosion processes, not only the classical erosion parameter must be considered, e.g. erosivity of rain, erodibility of the soil, slope, soil constituents etc., but even more the actual structural status of soil, like pore size distribution, infiltration rate, hydraulic conductivity, and particular crop protection practices like mulching.

The tillage Pesticide residues in the bottom sediments of the surface water systems may be influenced by a number of factors including runoff potential and intrinsic properties of the pesticides (Krueger *et al.,* 1999)

- Dispersion
- Solid particles adsorption
- Aggregates adsorption

Risk for surface water systems!

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(Eriksson *et al.,* 2007, Warren et al, 2003; Krueger *et al.,* 1999; Peruzzo *et al.,* 2008; Warnemuende *et al.,* 2007; Siimes et al., 2006; Widenfalk *et al.,* 2007)

Leaching-preferential flows. The sources and transport routes of pesticides to groundwater are multifaceted. They can include non-point sources such as agriculture, with pesticide leaching from top soil via:

- Matrix-flow in sandy aquifers
- Preferential flow or macropore flow in eg tills
- Surface water recharge of groundwater through "leaky streams"
- Soil cracks
- Intra-aggregate pores
- Inter-aggregate pores

In the study of Rueppel ML *et al.,* (1977), glyphosate was considered as pesticide I class and thereby posses no propensity for leaching. On the other hand, in certain soils and under different conditions, there is a risk for groundwater contamination as it is shown in some other investigations (Albrechsten *et al.,* 2001; Landry *et al.,* 2005; Papiernik SK, 2001; Stenrød M *et al*., 2007). Degradation potential of pesticide is lower in aquifers than in top soil.

Influence of glyphosate on shallow aquifers/aquatic/marine ecosystems. Influence of glyphosate on different water organisms in water systems was already in various investigations shown (Warren *et al.,* 2003;Feng *et al.,* 1990; Tsui and Chu, 2007; Peruzzo *et al.,* 2008; Amorós et al., 2007; Widenfalk *et al.,* 2007). There is still a need for more data for better understanding the influence and behavior of glyphosate and metabolites in water bodies. Interaction of these pollutants with different organisms in water ecosystems should be more investigated:

- In shallow aquifer ecosystems;
- In different aquatic ecosystems, influence on plants and microbes;
- Influence on marine plants and microbes.

The importance of investigation of the Glyphosate behavior in soil. Better understanding of Glyphosates behavior is needed (e.g. adsorption conditions, environmental influence, specific soil parameters, soil microbes behavior).
Based on this knowledge time dependent adsorption, degradation rates and consequently risks for surface and groundwater involved can be estimated.

Multi component analyses of organic pollutants. There is a need of methodological approaches of multi component analyses to measure the trace concentrations in different ecosystems and rate of pollutant transformation in soil (Crommentuijn *et al.,* 2000; Papiernik SK, 2001). These methods should be used for:

- Field measurements for monitoring purposes
- Laboratory measurements under fully controlled conditions.

References

ALASDAIR H. NEILSON AND ANN-SOFIE ALLARD (2008) Environmental degradation and transformation of organic chemicals. CRC Press, Boca Raton, Florida, p. 51-57, 599-637.

ALBRECHSTEN H-J, MILLS MS, AAMAND J, BJERG PL (2001) Degradation of herbicides in shallow Danish aquifers: an integrated laboratory and field study. Pest Manag Sci 57:341-350.

AMORÓS I, ALONSO JL, ROMAGUERA S AND CARRASCO JM (2007) Assessment of toxicity of a glyphosate-based formulation using bacterial systems in lake water. Chemosphere 67:2221-2228.

ANDREU V, PICO Y (2004) Determination of pesticides and their degradation products in soil: critical review and comparison of methods. Trends in Analytical Chemistry, 23.

ARBELI Z , FUENTES CL (2007) Accelerated biodegradation of pesticides: An overview of the phenomenon, its basis and possible solutions; and a discussion on the tropical dimension. Crop Protection 26:1733-1746.

BALTHAZOR TM , HALLAS LE (1985) Glyphosate-degradaing microorganisms from industrial activated sludge. Applied and Environmenatl Microbiology, 51-2:432-434.

BAYLIS AD (2000) Why glyphosate is a global herbicide: strengths, weaknesses and prospects. Pest Manag Sci **56**:99-308.

BLUME E, BISCHOFF M, REICHERT JM, MOORMAN T, KONOPKA A, TURCO RF (2002) Surface and subsurface microbial biomass, community structure and metabolic activity as a function of soil depth and season. Applied Soil Ecology 20, 171-181.

CROMMENTUIJN T, SIJM D, DE BRUIJN J, VAN LEEUWEN K, VAN DE PLASSCHE E (2000) Maximum permissible and negligible concentrations for some organic substances and pesticides. Journal of Environmental Management 58, 297-312.

DICK RE, QUINN JP (1995) Control of glyphosate uptake and metabolism in *Pseudomonas* sp. 4ASW. FEMS Microbiology Letters 134, 177-182.

DYHRMAN ST, CHAPPELI PD, HALEY ST, MOFFETT JW, ORCHARD ED, WATERBURY JB, WEBB EA (2006) Phosphonate utilization by the globally important marine diazotroph *Trichodesmium*. Nature Letters Vol. 439, doi: 10.1038/nature04203

EBERBACH P (1997) Applying non-steady-state compartmental analysis to investigate the simultaneous degradation of soluble and sorbed glyphosate (N-(Phosphonomethyl)glycine) in four soils. Pestic. Sci. 52:229-240.

ERIKSSON E, BAUN A, MIKKELSEN PS, LEDIN A (2007) Risk assessment of xenobiotics in stormwater discharged to Harrestrup Å, Denmark. Desalination 215, 187-197.

FENG JC, THOMPSON DG, REYNOLDS PE (1990) Fate of Glyphosate in a Canadian Forest Watershed. 1. Aquatic Residues and Off-Target Deposit Assessment. J. Agric. Food Chem. 38:1110-1118.

FENNER N, FREEMAN C, REYNOLDS B (2005) Hydrological effects on the diversity of phenolic degrading bacteria in a petland: implication for carbon cycling. Soil Biology & Biochemistry 37:1277-1287.

FORLANI G, MANGIAGALLI A, MIELSEN E, SUARDI CM (1999) degradation of the phosphonate herbicide glyphosate in soil : evidence for a possible involvement of unculturable microorganisms. Soil Biology & Biochemistry 31:991-997.

FOSTER LJR, KWAN BH, VANCOV T (2004) Microbial degradation of the organophosphonate pesticide, Ethion. FEMS Microbiology Letters 240:9-53.

DOI: 10.6092/issn.2281-4485/3821

GHANEM A, BADOS P, ESTAUN AR, DE ALENCASTRO LF, TAIBI S, EINHORN J, MOUGIN C (2007) Concentrations and specific loads of glyphosate, diuron, atrazin, nonylphenol and metabolites thereof in French urban sewage sludge. Chemosphere 69:1368-1373.

GIMSING AL, BORGGAARD OK, JACOBSEN OS, AAMAND J, SØRENSEN J (2004) Chemical and microbiological soil characteristics controlling glyphosate mineralization in Danish surface soils. Applied Soil Ecology 27, 233-242.

HAGHANI K, SALMANIAN AH, RANJBAR B, ZAKIKHAN-ALANG K, KHAJEH K (2007) Comparative studies of wild type Escherichia coli 5-enopyruvylshikimate 3-phosphate synthase with three glyphosate-intensive mutated forms: Activity, stability and structural characterization. Biochim. Biophys. Acta (2007), doi: 10.1016/j.bbapap.2007.07.021

HAYES VEA, TERNAN NG, MCMULLAN G (2000) Organophosphonate metabolism by a moderately halophilic bacterial isolate. FEMS Microbiology Letters 186, 171-175.

JACOB GS, GARBOW JR, HALLAS LE; KIMACK NM, KISHORE GM, SCHAEFER J (1988) Metabolism of glyphosate in *Psedumonas sp*. Strain LBr. Applied and Environemental Microbiology Vol. 54, No. 12, 2953-2958.

KISHORE GM, JACOB GS (1987) Degradation of glyphosate by Pseudomonas sp. PG2982 via a Sarcosine Intermediate. The Journal of Biological Chemistry Vol. 262, No. 25, 12164-12168.

KOOLS SAE, VAN ROOVERT M, VAN GESTEL CAM, VAN STRAALEN NM (2005) Glyphosate degradation as a soil health indicator for heavy metal polluted soils. Soil Biology & Biochemistry 37, 1303-1307.

KRZYSKO-LUPICKA T, SUDOL T (2007) Interactions between glyphosate and autochthonous soil fungi surviving in aquaeous solution of glyphosate. Chemosphere, doi: 10.1016/j.chemosphere.2007.11.006

KRZYSKO-LUPICKA T, STROF W, KÚBS K, SKORUPA M, WIECZOREK P, LEJCZAK B, KAFARSKI P (1997) The ability of soil-borne fungi to degrade organophosphonate carbon-to.phosphorus bonds. Appl. Microbial Biotechnol. 48, 549-552.

KRUEGER J, PETERSON M, LUNDGREN E (1999) Agricultural inputs of pesticide residues to stream and pond sediments in a small catchment in southern Sweden. Bull. Environ. Contam, Toxicol. 62:55-62.

LANDRY D, DOUSSET S, FOURNIER J-C, ANDREUX F (2005) Leaching of glyphosate and AMPA under two soil management practices in Burgundy vineyards (Vosne-Romanée, 21-France). Environmental Pollution 138:191-200.

LIPOK J, OWSIAK T, MLYNARZ P, FORLANI G , KAFARSKI P (2007) Phosphorus NMR as a tool to study mineralization of prganophophonates - The ability of *Spirulina* spp. To degrade glyphosate. Enzyme and Microbial Technology 41:286-291.

LIU C-M, MCLEAN PA, SOOKDEO CC, CANNON FC (1991) Degradation of the herbicide glyphosate by members of the family Rhizobiaceae. Applied and Environmental Microbiology 57/6:1799-1804.

LOCKE MA, ZABLOTOWICZ RM (2004) Pesticides in Soil – Benefits and Limitations to Soil Health. Managin Soil Quality: Challenges in Modern Agriculture. Eds Schjønning, Elmholt S and Christensen BT. CAB International 239-260.

MAMY L, BARRIUSO E ,GABRIELLE (2005) Environmental fate of herbicides trifularin, metazachlor, metamitron and sulcotrione compared with that of glyphosate, a substitute broad spectrum herbicide for different glyphosate-resistant crops. Pest Manag Sci 61, 905-916.

MATTHIES M, WITT J, KLASMEIER J (2007) Determination of soil biodegradation half-lives from simulation testing under aerobic laboratory conditions: A kinetic model approach. Environ. Pollut., doi: 10.1016/j.envpol.2007.12.040

MCMULLAN G, QUINN JP (1993) The utilization of aminoalkylphosphonic acids as sole nitrogen source by an environmental bacterial isolate. Letters in Applied Microbiology 17:35-138.

MENTLER A, PAREDES M AND FUERHACKER M (2007) Adsorption of glyphosate to Cambisols, Podzol and silica sand. Poster presentation on COST 869.

Nicholls PH (1991) Organic contaminants in soils and groundwaters. In: Jones, K.C. (Ed.), Organic Contaminants in the groundwater, Elsevier Applied Science, London, p. 87-132.

Nowack B (2003) Review Environmental chemistry of phosphonates. Water Research 37:2533-2546.

Obojska A, Lejczak B and Kurbak M (1999) Degradation of phosphonates by streptomycete isolates. Appl. Microbiol. Biotechnol. 51, 872-876.

Obojska A, Ternan NG, Lejczak B, Kafarski P and McMullan G (2002) Organophosphonate Utilization by the Thermophile Geobacillus caldoxylosilyticus T20. Applied and Environmental Microbiology 68-4:2081- 2084.

PAPIERNIK SK (2001) A review of *in situ* measurement of organic compound transformation in groundwater. Pest Manag Sci 57:325-332.

PERUZZO PJ, PORTA AA, RONCO AE (2008) Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in north pampasic region of Argentina. Environ. Pollut. Doi: 10.1016/j.envpol.2008.01.015

PIPKE R, AMRHEIN N (1988) Degradation of the phosphonate herbicide glyphosate by Arthrobacter atrocyaneus ATCC 13752. Applied and Environmental Microbiology 54-5:1293-1296.

PITTER P, CHUDOBA J (1990) Biodegradability of Organic Substances in the Aquatic Environment. CRC Press, Boca Raton, FL (1990), p. 167-178.

RODRÍGEZ-CRUZ MS, JONES JE, BENDING GD (2006) Field-scale study of the variability in the pesticide biodegradation with soil depth and its relationship with soil characteristics. Soil Biology & Biochemistry 38:2910-2918.

RUEPPEL ML, BRIGHTWELL BB, SCHAEFER J, MARVEL JT (1977) Metabolism and degradation of glyphosate in soil and water. J. Agric. Food Chem., 25-3: 517-528.

SCHNURER Y, PERSSON P, NILSSON M, NORDGREN A, GIESLER R (2006) Effects of surface sorption on microbial degradation of glyphosate. Environ. Sci. technol. 40: 4145-4150.

SCHWARZBAUER J (2005) Organic contaminants in riverine and groundwater systems. Springer Berlin Heidelberg New York, p. 1-23.

SIIMES K, RÄMÖ S, WELLING L, NIKUNEN U, LAITINEN P (2006) Comparison of the beahviour of the three herbicides in a field experiment under bare soil conditions. Agricultural Water Management 84:53-64.

SINGH BK, WALKER A, WRIGHT DJ (2005) Cross-enhancement of accelerated biodegradation of organophosphorus compounds in soils: Dependance on structural similarity of compounds. Soil Biology & Biochemistry 37: 1675-1682.

SOULAS G., LAGACHERIE B. (2001) Modelling of microbial degradation of pesticides in soils. Biol Fertil Soils 33:551-557.

SØRENSEN SR, SCHULTZ A, JACOBSEN OS, AAMAND J (2006) Sorption, desorption and mineralisation of the herbicides glyphosate and MPCA in samples from two Danish soil and subsurface profiles. Environmental Pollution 141:184-194.

SMITH RN (1991) Developments in fuel microbiology. In: Rossmoore, H.R., Editor, , 1991. *Biodeterioration and Biodegradation 8*, Elsevier, London, p. 112–124

STENRØD M, CHARNAY M-P, BENOIT P, EKLO OM (2006) Spatial variability of glyphosate mineralization and soil microbial characteristics in two Norwegian sandy loam soils as affected by surface topographical features. Soil Biology & Biochemistry 38:962-971.

STENRØD M, EKLO OM, CHARNAY M-P, BENOIT P (2005) Effect of freezing and thawing on microbial activity and glyphosate degradation in two Norwegian soils. Pest Manag Sci 61:887-898.

STENRØD M, PERCEVAL J, BENOIT P, ALMVIK M, BOLLI RI, EKLO OM, SVEISTRUP TE, JENS KVAERNER (2007) Cold climatic conditions; Effects on bioavailability and leaching of the mobile pesticide metribuzin in a silt loam soil in Norway. Cold Regions Science and Technology, doi: 10.1016/j.coldregions.2007.06.07

TERNAN NG, MC GRATH JW, MC MULLAN G , QUINN JP (1998) Review: Organophosphonates: occurance, synthesis and biodegradation by microorganisms. World of Journal of Microbiology & Biotechnology 14: 635-647.

TSUI MTK, CHU LM (2008) Environmental fate and non-target impact of glyphosate-based herbicide (Roundup®) in a subtropical wetland. Chemosphere 71: 439-446.

TYKVA R. (1998) Selection of a pesticide with low environmental impact. Ecotoxicology and environmental safety 40:94-96.

VAN AGTEREN MH, KEUNING S , JANSSEN DB (1998) Handbook on biodegradation and biological treatment of hazardous organic compounds. Luwer Academic Publishers Dordrecht/Boston/London, p. 3-12.

VATHANOMSAT P ,BROWN KA (2007) Isolation and mutation of recombinant EPSP synthase from pathogenic bacteria Pseudomonas aeruginosa. Process Biochemistry 42:592-598.

WARNEMUENDE EA, PATTERSON JP, SMITH DR , HUANG C-H (2007) Effects of tilling no-till soil on losses of atrazine and glyphosate to runoff water under variable intensity simulated rainfall. Soil & Tillage Research 95:19-26.

WARREN N, ALLAN IJ, CARTER JE, HOUSE WA , PARKER A (2003) REVIEW PESTICIDES AND OTHER MICRO-ORGANIC CONTAMINANTS IN FRESHWATER SEDIMENTARY ENVIRONMENTS-A REVIEW. APplied Geochemistry 18:159-194.

WIDENFALK A, BERTILSSON S, SUNDH I, GOEDKOOP W (2007) effects of pesticides on community composition and activity of sediment microbes – responses at various levels of microbial community organization. Environ. Pollut., doi: 10. 1016 /j.envpol. 2007.07.003.

ZABLOTOWICZ RM, LOCKE MA, KRUTZ LJ, LERCH RN, LIZOTTE RE, KNIGHT SS, GORDON RE, STEINRIEDE RW (2006) Influence of watershed system managemen on herbicide concentrations in Missisippi Delta oxbow lakes. Science of the Total Environment 370:552-560.

ZARANYIKA MF, NYANDRO MG (1993) Degradation of Glyphosate in the aquatic environment: An enzymatic kineti model that takes into account microbial degradation of both free and colloidal (or sediment) particle adsorbed glyphosate. J. Agric. Food Chem. 41:838-842.