MTT SCIENCE 3

Fate of the organophosphate herbicide glyphosate in arable soils and its relationship to soil phosphorus status

Doctoral Dissertation

Pirkko Laitinen

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Abstract

Glyphosate [(N-(phosphonomethyl) glycine)] is one of the world's most widely used herbicides. In Finland, glyphosate accounted for 66% of herbicide-active ingredients sold in 2007. In recent years, the pattern of glyphosate use in cereal cultivation has changed from post-harvest spraying every second or third year followed by autumn ploughing to annual spring and/or autumn application when reduced tillage cultivation or no till is used instead of ploughing. For intensive use it is important to understand the fate of glyphosate in soils. This study was undertaken to unravel the factors affecting its movement, sorption, persistence and leachability in different Finnish soils to create a sound basis for risk assessment.

In soil, the movement of glyphosate is retarded by sorption reactions through its phosphonate group on Al and Fe oxide/hydroxides, and the broken surfaces of silicate minerals. This reaction pattern means that glyphosate competes with phosphate for the same sorption sites. On the other hand, phosphate can displace adsorbed glyphosate from sorption sites, resulting in an increased leaching risk.

As a systemic herbicide, glyphosate is first absorbed by foliage and then translocated throughout the plant via the phloem and further transported to metabolic sinks such as meristems and roots. From the roots it can be released to the soil when dead roots decompose. The translocation within the plant can be quite rapid and glyphosate may end up in the root zone in deeper soil layers also in circumstances where no transport through the soil matrix occurs. In our study, more than 12% of the applied glyphosate was found in the roots. Thus, translocation through plants and residues in dead root mass have a significant role in controlling the fate of glyphosate in soil and should be included both in leaching risk assessments and pesticide fate models.

Field experiments indicated rather long persistence of glyphosate in Finnish soils low in soil test P.

The key soil factors promoting the persistence and reducing the leaching of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) appeared to be low P status and high Al and Fe oxide contents in soil, leading to low degree of P saturation (DPS) and to reduced biodegradability as a result of strong sorption. The results revealed that glyphosate adsorption decreases with increasing phosphorus (P) status of soil (acid ammonium acetate-extractable P (P_{AC})). The adsorbed glyphosate was 11% lower in soils with an excessive P_{AC} level than in soils low in P_{AC}, and the mobility of glyphosate increased drastically at the excessive P level. The strong and rather irreversible adsorption found in the sorption tests suggested that the risk of glyphosate leaching through the soil matrix is minor when the soil P status is low. A preliminary test of the degree of P saturation (DPS), P_{AC} and K_F values with the Finnish pesticide mobility classes suggests that the critical DPS value for glyphosate movement might be near the critical values for P leaching.

Because there is a good correlation between DPS and P_{AC}, this further suggests that the soil P status might be useful in environmental risk assessment for glyphosate. Such a risk indicator would be accessible at farm level in the vast majority of Finnish farms, as a result of a very high degree of participation in the Finnish Agri-Environmental Programme that requires soil testing.

Climatic conditions, such as dry summers and cold winters, reduced the degradation rate. Glyphosate and AMPA showed a clear over-winter persistence even when the glyphosate applications were done in June-July the previous year. Thus, repeated applications without deep tillage may lead to the accumulation of glyphosate and AMPA on the soil surface. Depending on soil management, autumn application may further increase the risk for environmental pollution through losses by surface runoff or subsurface leaching. Application in late autumn should be critically evaluated and possibly restrictions should be set on this practice for the most critical fields.

Key words:
AMPA, environmental risk, glyphosate, leaching, mobility, phosphorus status, sorption, translocation

Glyfosaatin käyttäytyminen peltomaassa ja pellon fosforitason vaikutus siihen

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Tiivistelmä

Glyfosaatti [(N-(phosphonomethyl) glycine)] on yksi maailman eniten käytetyistä rikkakasvien torjunta-aineista (herbisideistä). Suomessa sen myynti vastasi noin 66 prosenttia vuonna 2007 myydystä herbisideistä. Viljelymenetelmät ja niiden myötä myös glyfosaatin käyttötavat ovat viime vuosina muuttuneet. Perinteisen, kolmen – neljän vuoden välein tehdyn syysruiskutuksen ja sitä seuranneen pellon kynnön lisäksi kevyemmät muokkausmenetelmät ovat yleistyneet. Niissä glyfosaatia käytetään vuosittain kevätkylvön yhteydessä ja usein myös syksyllä. Intensiivisen ja yhä kasvavan käytön vuoksi on tärkeää tunnistaa ne tekijät, jotka vaikuttavat glyfosaatin käyttäytymiseen maassa ja etsiä välineitä kulkeutumis-, kertymis- ja huuhtoutumisriskien arviointiin.

Glyfosaatti kuuluu orgaanisiin fosforivalmisteisiin, joten se voi sitoutua maassa samoille paikoille kuin fosfori, eli alumiini- ja rautaoksideihin ja -hydroksideihin. Glyfosaatti kilpaileekin sitoutumispaikoista fosforin kanssa. Vahvempana kilpailijana fosfori voi estää glyfosaatin sitoutumisen tai syrjäyttää jo sitoutuneen glyfosaatin.

Glyfosaatti on systeeminen herbisidi, jonka teho perustuu siihen, että se imeytyy ensin lehtiin ja kulkeutuu sitten kasvissa jakaantumiskykyisiin soluihin, kuten juurten kärkipisteisiin ja estää siellä solunjakautumisen. Glyfosaatti ei hajoa kasvissa, tai sen hajoaminen on minimaalista ja sitä voi kertyä juuristoon huomattavia määriä. Juurien hajotessa glyfosaati vapautuu maahan, jossa se hajoaa mikrobien toimesta. Kulkeutuminen kasvin kautta syvällekin maahan on nopeaa ja se voi tapahtua myös kuivissa olosuhteissa, joissa kulkeutuminen maaperässä ei ole mahdollista.

Tässä työssä tutkittiin glyfosaatin sitoutumista peltomaahan ja maan fosforitason vaikutusta sitoutumiseen laboratoriotestien avulla. Glyfosaatin pysyvyyttä (hajoamista), kulkeutumista maaprofiilissa ja huuhtoutumista pellolta tutkittiin peltokokeissa ja kulkeutumista kasvin kautta astia- ja peltokokeissa.

Ensimmäisessä laboratoriotestissä määritettiin glyfosaatin sitoutumiskertoimet erilaisiin peltomaihin ja testattiin maan ominaisuuksien vaikutuksia sitoutumiseen. Sitoutumiskertoimien perusteella glyfosaatti voitiin luokitella maassa joko heikosti kulkeutuvaksi tai kulkeutumattomaksi yhdisteeksi. Mikään testatuista maan ominaisuuksista (lajitejakauma, orgaanisen hiilen määrä, pH, oksidipitoisuus, epäorgaaninen fosfori ja viljavuusfosforin arvo) ei yksinään selittänyt sitoutumista.

Toisessa laboratoriotestissä tutkittiin maan fosforitason vaikutusta glyfosaatin sitoutumiseen. Tavoitteena oli selvittää, voidaanko

viljavuusfosforin avulla arvioida glyfosaatin kulkeutuvuusriskiä.

Glyfosaatin kulkeutuvuus kasvoi huomattavasti maan fosforiluvun kasvaessa. Glyfosaatin sitoutuminen väheni ja sidos heikkeni maan fosforinluvun kohotessa. Sitoutuneen glyfosaatin määrä pieneni 11 prosenttia siirryttäessä matalalta fosforitasolta korkealle tasolle. Voidaankin todeta, että maan fosforitson kasvaessa glyfosaatin sitoutuminen heikkenee ja sen kulkeutumis- ja huuhtoutumisriskit kasvavat.

Kenttäkokeissa seurattiin glyfosaatin ja sen hajoamistuotteen, aminometylifosforihapon (AMPA), hajoamista, kulkeutumista maaprofiilissa ja huuhtoutumista pinta- ja salaojavesien mukana.

Glyfosaatin pysyvyyteen ja kulkeutuvuuteen vaikuttivat eniten maaperän alhainen fosforitila, korkea alumiini- ja rautaoksidipitoisuus ja vapaiden oksidipintojen määrä, käsittely ajankohta (kesä – syksy) sekä sääolosuhteet (kuiva kasvukausi ja kylmä talvi). Tulokset osoittavat, että glyfosaatin huuhtoutumisriski on pieni silloin kun maan viljavuusfosforin arvo on pieni. Toisaalta tiukka sitoutuminen maahan hidastaa glyfosaatin hajoamista ja voi johtaa jäämien kertymiseen maahan, erityisesti silloin kun glyfosaattia käytetään toistuvasti.

Tulokset osoittavat, että glyfosaatin kertyvyys- ja huuhtoutumisriskin arviointiin voidaan käyttää samoja tekijöitä, jotka määrittävät fosforin käyttäytymistä maassa. Viljavuusfosfori voisi olla käyttökelpoinen ja ekonominen väline tähän arviointiin. Suomessa pellon fosforitasoa seurataan säännöllisesti, joten meillä on käytettävissä laaja aineisto sekä alueellista että tilatason riskinarviointia varten.

Glyfosaatti hajoasi hitaasti alhaisen fosforitason maassa ja sitä ja AMPA:a oli maassa vielä seuraavana keväänä, vaikka käsittely olisi tehty alkukesästä. Toistuva käyttö ilman että maa kynnetään johtaa glyfosaatin kertymiseen pellon pintaan. Syyskäsittelyn jälkeen hajoaminen on hidasta ja, muokkauksesta riippuen, voi johtaa huuhtoutumiseen joko pinta- tai salaojavesien mukana. Syyskäsittelyä tuleekin arvioida kriittisesti ja myös rajoittaa sitä ainakin kriittisimmillä alueilla.

Astia- ja kenttäkokeissa glyfosaattin kulkeutuminen kasvissa juuristoon oli merkittävää. Juuristossa sitä oli yli 12 prosenttia käytetystä määrästä. Tämä tutkimus on ensimmäinen, jossa yhteys maassa havaittuihin jäämiin ja kulkeutumiseen kasvissa on osoitettu. Kulkeutumien kasvissa tuleekin huomioida arvioitaessa glyfosaatin ympäristöriskejä ja se tulee liittää tärkeänä tekijänä myös matemaattisiin käyttäytymismalleihin.

Avainsanat:
glyfosaatti, huuhtoutuminen, kertyminen maahan, kulkeutuminen kasvissa, sitoutuminen maahan, ympäristöriskit

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ABBREVIATIONS

ADI	Acceptable Daily Intake
Al_{OX}	aluminium oxide/hydroxide
AMPA	aminomethylphosphonic acid
EPSP	enolpyruvylshikimate phosphate
Fe_{OX}	iron oxide/hydroxide
GLY	glyphosate [(N-(phosphonomethyl)glycine)]
GLU	glufosinate-ammonium
GMO	geneticaly modified organism
DL	detection limit
DPS	degree of phosphorus saturation
DT50	degradation time required for 50% of substance to be degraded
DT90	degradation time required for 90% of substance to be degraded
FAO	Food and Agriculture Organization of the United Nations
K_d	sorption coefficient, partitioning of a substance between liquid and solid phases at equilibrium
K_F	Freundlich sorption coefficient
K_{FOC}	Freundlich sorption coefficient based on soil organic carbon
K_{CLAY}	sorption coefficient based on soil clay fraction
K_{OC}	sorption coefficient based on soil organic carbon
K_{OW}	n-octanol/water partion coefficient
K_{sat}	saturated hydraulic conductivity in undisturbed soil
MPC_{water}	Maximum Permissible Concentration for aquatic ecosystems
OC	organic carbon
P_{AC}	phosphorus extracted with acid ammonium acetate
P_{TOT}	total phosphorus in soil
P_W	phosphorus extracted with water
POEA	polyethoxylate tallowamine
PO_4-P	dissolved orthophosphate phosphorus
RSD	relative standard deviation
TP_{WATER}	total phosphorus in water
TS	total solids
WHO	World Health Organization

LIST OF ORIGINAL PUBLICATIONS

This thesis is a summary and discussion of the following articles, which are referred to in the text by their chapter numbers:

Chapter 2	Autio, S., Siimes, K., Laitinen, P., Rämö, S., Oinonen, S. & Eronen L. 2004. Adsorption of sugar beet herbicides to Finnish soils. *Chemosphere* 55:215–226.
Chapter 3	Laitinen, P., Siimes, K., Rämö, S., Jauhiainen, L., Oinonen, S., Eronen, L. & Hartikainen, H. 2008. Soil phosphorus status in environmental risks assessment for glyphosate and glufosinate-ammonium. *Journal of Environmental Quality* 37: 830–838.
Chapter 4	Laitinen, P. Siimes, K., Eronen, L., Rämö, S., Welling, L., Oinonen, S., Mattsoff, L. & Ruohonen-Lehto, M. 2006. Fate of the herbicides glyphosate, glufosinate-ammonium, phenmedipham, ethofumesate and metamitron in two Finnish arable soils. *Pest Management Science* 62: 473–491.
Chapter 5	Laitinen, P., Rämö, S., Nikunen,U., Jauhiainen L., Siimes, K. & Turtola, E. 2009. Glyphosate and phosphorus leaching and residues in boreal sandy soil. Accepted 09.02.2009 *Plant and Soil*. DOI 10.1007/s11104-009-9935-y.
Chapter 6	Laitinen, P., Rämö, S. & Siimes, K. 2007. Glyphosate translocation from plants to soil – does this constitute a significant proportion of residues in soil. *Plant and Soil* 300: 51–60.

The author's contribution in joint publications

Chapter 2	Pirkko Laitinen planned the experiment with Sari Autio and Katri Siimes. Pirkko Laitinen conducted the experiment and did the data processing together with Katri Siimes. Sari Rämö was responsible for measurement of adsorption coefficients and Liisa Eronen for other soil analyses. Pirkko Laitinen interpreted the results and wrote the paper with the co-authors, Sari Autio having the main responsibility.
Chapter 3	Pirkko Laitinen planned the experiment with Katri Siimes and Helinä Hartikainen, and conducted the experiment and calculated the data with Sari Rämö, and interpreted the results with Katri Siimes and Helinä Hartikainen. Sari Rämö was responsible for measurement of adsorption coefficients and Liisa Eronen for phosphorus analyses. Lauri Jauhiainen did the statistical analysis and developed the model. Pirkko Laitinen was mainly responsible for writing the paper.
Chapter 4	Pirkko Laitinen planned the experiment with Liisa Eronen, Katri Siimes and Marja Ruohonen-Lehto. The experiment was conducted by Pirkko Laitinen (main responsibility), Katri Siimes and Liisa Eronen. Liisa Eronen was responsible for field experiment practices and for soil analyses. Sari Rämö, Leena Welling and Seija Oinonen carried out the herbicide residue analysis. Pirkko Laitinen and Katri Siimes were responsible for data processing and interpretation of the results. Pirkko Laitinen and Katri Siimes wrote the paper together with the other co-authors. Katri Siimes was responsible for the pesticide dissipation calculations.
Chapter 5	Pirkko Laitinen planned and conducted the experiment with Eila Turtola. Unto Nikunen was responsible for field experiment practices. Lauri Jauhiainen did the statistical analysis. Pirkko Laitinen was mainly responsible for data processing, interpreting the results with the co-authors and for writing the paper.
Chapter 6	Pirkko Laitinen planned and conducted the experiment and calculated the results with Sari Rämö. Pirkko Laitinen interpreted the results with Katri Siimes who was responsible for the pesticide modelling. Pirkko Laitinen was mainly responsible for writing the paper.

Contents

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CHAPTER 1
General introduction

General introduction

1.1 Pesticides in agriculture (Overview)

1.1.1 Sales and use in Finland

Total sales of active ingredients of pesticides in 2007 were 1.7 tonnes, the sales of commercial products being 4.5 tonnes. The sales of herbicides accounted for 80% of the total sales of active ingredients. The sales of cereal herbicides were sufficient for a single treatment of 1,070,000 hectares, equivalent to 80% of the cereal area cultivated in 2007 (Evira 2008).

1.1.2 Environmental fate

In field conditions the dissipation of pesticides in the soil consists of chemical and microbiological degradation, as well as movement and leaching with surface and subsurface waters. Also photodegradation and losses by volatilization or wind drift, or by runoff and erosion, may occur (Figure 1). The main processes affecting the fate of pesticides in the soil are their degradation and sorption (adsorption-desorption) to the soil.

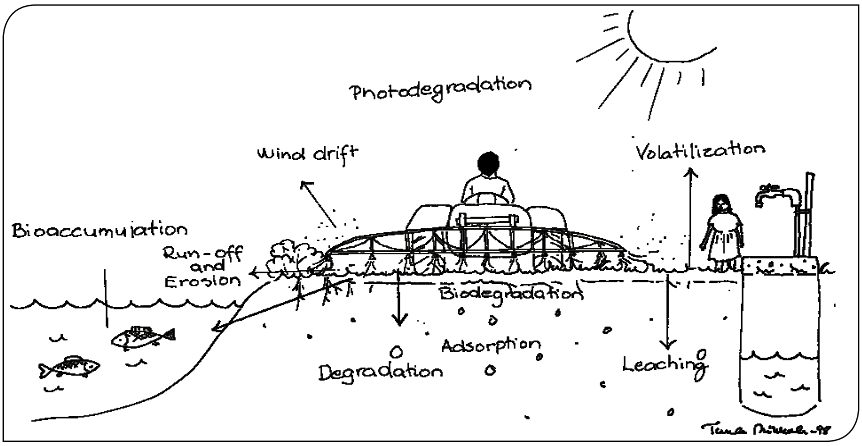


Figure 1.1. Environmental fate of pesticides. (Drawing of Tiina Mikkola 1998).

1.2 Terminology used in pesticide reactions

1.2.1 Degradation

The degradation rate of pesticides in soil can be described by their half-life or dissipation time (DT50 or DT90) (the time required for 50% or 90% of the compound to degrade or dissipate). Field dissipation includes, in addition to degradation, leaching losses, photodegradation and volatilization. Soil and pesticide properties, microbiological activity and climatic conditions affect the field dissipation rates of pesticides. Climatic factors, such as temperature and moisture, are crucial in terms of microbial activity (e.g. Insam 1990) and, consequently, in pesticide degradation.

1.2.2 Sorption

Soil particles bind (adsorb) pesticides by physical and chemical bonds. The molecular structure of the pesticide determines its sorption affinity to soil particles. Different sorption mechanisms were originally presented by Giles et al. (1960) and were later demonstrated by several publications (e.g. Sparks 1989 pp. 128–143; McBride 1994, p. 139). Adsorption may be either reversible or irreversible, depending on the properties of both the pesticide and the soil. The difference between reversibly aged and irreversibly bound residues is not clear-cut but, in general, bound residues are considered as the non-extractable fraction of chemicals (Gevao et al. 2000). Strong sorption to soil particles reduces the risk of leaching (Walker et al. 2005) but, on the other hand, it often retards the degradation of the pesticide and can lead to its accumulation in the soil and the formation of bound or aged residues. From an ecotoxicological perspective binding can reduce the toxicity of a compound by decreasing its interactions with soil biota (Gevao et al. 2000).

1.2.3 Equilibrium and non-equilibrium sorption

Predictions of pesticide sorption in soil are generally based on equilibrium thermodynamic processes where the pesticide equilibrium state between liquid and solid phases is assumed to be reached rapidly. In contrast to such an equilibrium state, time-dependent sorption is a non-equilibrium (kinetic) process where the adsorption becomes less or non-reversible with time (Walker 1987; Strek et al. 2007). This time-dependent sorption is also called aging. Sharer et al. (2003) stated that the formation of aged residues of chlorobenzene was dependent on the pesticide-soil contact time and that the non-desorbable fraction of the chemical increased with increasing aging. Van Beinum et al. (2006) in a review concluded that aging is likely to be caused by a combination of (i) diffusion of the pesticide through larger pores between soil aggregates, (ii) solute diffusion into smaller pores inside soil aggregates, and (iii) slow diffusion at a very small scale into the matrix of organic and mineral sorbents.

1.2.4 Determination of equilibrium adsorption

Adsorption coefficients are used in the mobility classification of pesticides in order to compare the leaching characteristics of different pesticides in different soils. They are needed as input values in simulation models for pesticide fate and environmental risk assessment.

The linear adsorption coefficient (K_d) represents the partitioning of the substance between liquid (C_l) and solid phases (S) in a state of equilibrium (Equation 1 and Figure 2). The empirical Freundlich sorption isotherm (Equation 2) takes into account the non-linearity of sorption with increasing concentration. If the value of the Freundlich exponent (1/n) is one, adsorption is linear. If the exponent value is less than one, the proportion of adsorbed pesticide decreases as the concentration increases. The higher the K_F value, the higher the adsorption to soil. This means that the pesticide leaching risk increases as the K_F value decreases.

Linear partitioning:

$$S=K_dC \qquad \text{(Equation 1)}$$

Freundlich sorption isotherm:

$$S=K_FC^{1/n} \qquad \text{(Equation 2)}$$

where S is the sorbed amount (mg kg^{-1}) and C is the concentration in soil water (mg L^{-1}), K_F is the Freundlich sorption coefficient and 1/n is the Freundlich exponent. The adsorption coefficients based on the fraction of organic carbon content in the soil (K_{OC}) (Equation 3) are used in order to avoid the effect of soil properties on the adsorption coefficient value. The use of K_{OC} is based on an assumption that pesticides are adsorbed by organic carbon.

$K_{OC} = K_d / OC$ (Equation 3)

Like the K_{OC} values, the K_F values are also often calculated on the basis of soil organic carbon content (K_{FOC}). However, although K_{OC} and K_{FOC} may explain the behaviour of non-polar, non-ionic substances (i.e. substances having an affinity for soil organic matter), they are not suitable for polar, ionic or ionizable substances (e.g. glyphosate) which often have a high affinity for soil minerals as reviewed by Hermosin et al. (2000) and Borggaard and Gimsing (2008).

Hermosin et al. (2000) have also presented a pesticide adsorption coefficient for soils' clay fraction (K_{CLAY}), which has a similar basis to that of K_{OC} for organic carbon. The use of K_{CLAY} is based on the assumption that the clay fraction of the soil is the dominant factor controlling the sorption of polar pesticides. However, mostly the Freundlich sorption isotherm (K_F) or its modifications are used to describe sorption in a soil environment.

Figure 1. 2 demonstrates the influence of both pesticide properties (A) and soil properties (B) on the pesticide adsorption. Pesticide 1 adsorbs to soil to a greater extent than pesticide 2 (Figure 1. 2A). For example, at the concentration of 1 mg L^{-1} of pesticide in the solution phase there is a greater amount of pesticide 1 than pesticide 2 bound to the soil and, accordingly, more of pesticide 2 is in dissolved form and available for leaching. Metribuzine was more leachable and bioavailable in the Lammi soil than in the Loppi soil (Figure 1. 2B).

1.2.5 Reversibility of adsorption (desorption)

As discussed above, adsorption may be either reversible or irreversible depending on the properties of both the pesticide and the soil. Reversibility is tested in connection with the adsorption coefficient test. The adsorption coefficient test is continued as a desorption test and a desorption

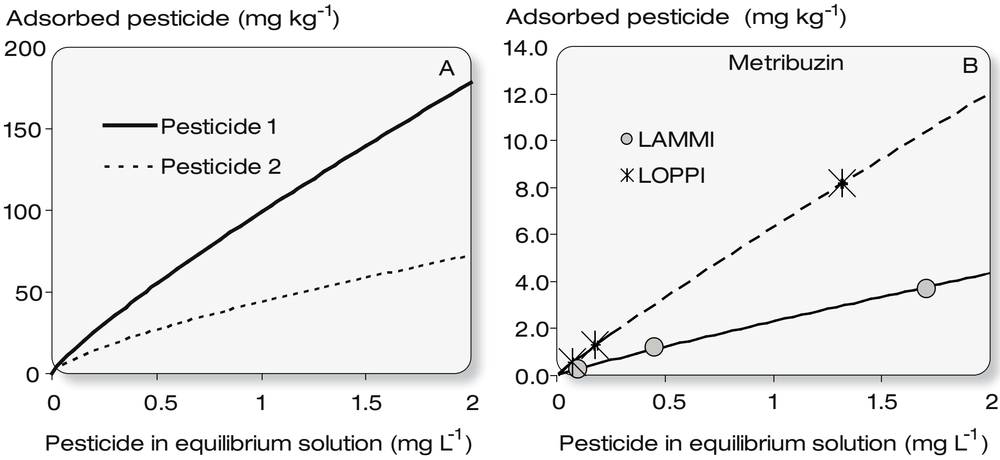


Figure 1.2. Adsorption isotherms for two different pesticides (A) in the same soil and metribuzin in two different soils (B). The Lammi soil was sandy and the Loppi soil sandy loam with high organic carbon content. (Figure B: Rämö (2008). Published by permission of MTT Agrifood Research Finland).

percentage of adsorbed pesticide is then calculated.

1.2.6 Factors affecting pesticide transport from agricultural soils

Factors that control the leaching losses of agrochemicals are their properties, weather patterns, precipitation, soil type and structure as well as the method and timing of pesticide application (Gentry et al. 2000). Pesticides can be transported as solutes or bonded to soil colloids. Both dissolved and particle-bonded forms can be transported through the soil by subsurface (percolation) and overland (runoff) flow. Subsurface flow ends up in drainage and groundwater, while the recipients of surface runoffs are open ditches, streams and lakes. In a field with good subsurface drainage systems the majority of leachates end up in drainage, and further to surface waters. However, part of the leachates may bypass the drainage system and leach to deeper soil layers, where pesticides can be adsorbed, degraded or transported towards groundwater. In uniform, unstructured soils (i.e. many sandy soils), water movement is described as matrix flow while in structured soils it is described as preferential flow (typical in clay soils). Preferential flow refers to uneven and often rapid movement of water and solutes through macropores, cracks between aggregates, root channels and wormholes, allowing much faster transport of pesticides than by matrix flow (Borggaard and Gimsing 2008).

Ploughing can increase the subsurface transport (Turtola et al. 2007) and the leaching risk of pesticides with subsurface drain flow (Laitinen 2000). In a study conducted on field-size lysimeters, pesticide losses in surface runoff water peaked during the snow melting and soil thawing period when the soil was not ploughed in the autumn, whereas after autumn ploughing pesticides were found only in the subsurface drain flow (Laitinen 2000). However, in another study by Fortin et al. (2002), where rapid pesticide movement to tile drains suggested that preferential flow was important in both conventional and reduced tillage, tillage practices had little influence on the pathway of pesticide transport.

Weather events, such as rainfall shortly after pesticide application, may be more critical for pesticide movement than climatic factors, such as average annual rainfall and temperature. Based on the results of a pesticide simulation study, Nolan et al. (2008) indicated that the majority of pesticide losses generally occurred with heavy rainfall events following autumn application on clay soil, for both surface runoff and drainage flow scenarios. They also found that the amount and timing of winter rainfall were important factors, whatever the application period was. These factors, regardless of the application period, interacted strongly with soil texture and pesticide persistence and mobility. Interestingly, the simulation test suggested that winter rainfall primarily would influence losses of less mobile and more persistent pesticides, whereas short-time rainfall and temperature would control leaching of more mobile pesticides. According to Strek et al. (2007), stronger adsorption over time has generally been found in soils of lower moisture content.

1.3 Glyphosate and its fate in the environment

1.3.1 Use and application practices

Glyphosate has been one of the world's most widely used herbicides since it was introduced on the market in 1974. In Finland, glyphosate accounted for 66% of herbicide-active ingredients sold in 2007 (Evira, 2008). Total sales of herbicides (including glyphosates) and glyphosates in Finland since 1976 are presented in Figure 1. 3.

A major upward trend in sales of glyphosate products prevailed in the 2000s. The increase in the use of glyphosate is partly due to changes in cultivation practice, especially to no-till or minimum tillage. In addition, the decreased price of glyphosate probably lowered the threshold for its use (Savela and Hynninen, 2004). In 2007, the sales of glyphosate were about 557 tonnes of active ingredient which would have been sufficient for a single treatment of 550,000 hectares or 25% of the total cultivated area of Finland (Evira 2007). In 2007 there were 31 commercial glyphosate products on the Finnish market.

In Finland, the use of glyphosate for all cereal cultivation is allowed in spring and after harvesting. Pre-harvest application (two weeks before harvesting) is allowed only in cattle feed production. The autumn application has been common practice. In recent years, the use of glyphosate in cereal cultivation has changed from post-harvest spraying every second or third year to annual spring or autumn application, or their combination when reduced tillage cultivation or no-till is used.

1.3.2 Chemical and physical properties of glyphosate

Glyphosate is non-volatile, does not degrade photochemically and is stable in air. Selected physico-chemical characteristics of glyphosate and its main metabolite AMPA (aminomethylphosphonic acid) are presented in Table 1.1.

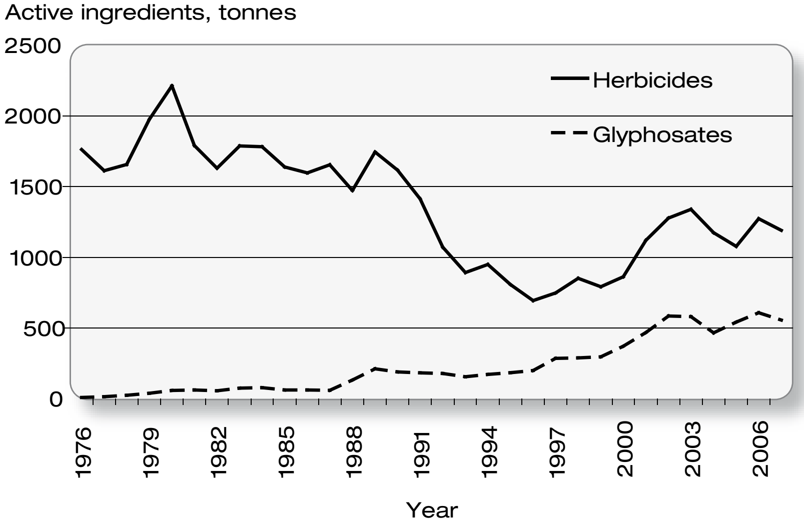
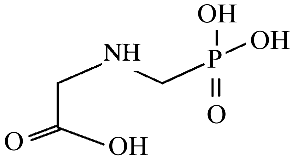
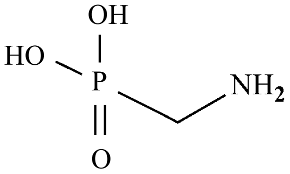


Figure 1.3. Sales of herbicides and glyphosates in 1976-2008 in Finland (tonnes of active ingredients). Savela 2009. Personal communication. (Published by permission of Evira.).

Table 1.1. Selected physico-chemical characteristics of glyphosate and AMPA.

Parameter	Glyphosate[a]	AMPA[b]
Chemical structure		
CAS number	1071-83-6	1066-51-9
Chemical name	[(N-phosphonomethyl)glycine)]	aminomethylphosphonic acid
Empirical formula	$C_3H_8NO_5P$	CH_6NO_3P
Molar mass	169.08	111.04
K_{OW} LogP	<-3.2 (pH 2-5, 20°C)	-2.17 (estimated)
Water solubility	11.6 g L^{-1} (20°C)	5.8 g L^{-1} (25°C)
Vapour pressure	$7.5x10^{-8}$ mm Hg	no data
pKa	pKa_1 0.8, pKa_2 3.0, pKa_3 6.0 and pKa_4 10.0	pKa_1 0.9, $pKa_{2,}$ 5.6, pKa_3 10.2
Freundlich sorption coefficient (K_F)	0.6-303 L kg^{-1}[c]	15.7-1570 L kg^{-1}).
Photodegradation in soil	not substantial over 31 days	
Photodegradation in water	DT50 <28 days	
Half-life in soil (field)	DT50 3-174 days	
Half-life in water	DT50 5-91 days	

[a]Tomling 2000.

[b]Traas and Smit 2003.

[c]Vereecken 2005.

1.3.3 Herbicidal function and translocation in plants

Glyphosate is a systemic, broad-spectrum herbicide that is first absorbed by foliage and then translocated throughout the plant via the phloem and further transported to metabolic sinks such as meristems and roots. Translocation has been shown to take place both in genetically modified and non-modified plants (Feng et al. 1999; Hetherington et al. 1999). The mechanism by which glyphosate is toxic to plants has been reported in detail, e.g. in Cole (1985) and Franz et al. (1997).

Glyphosate inhibits plant growth by inhibiting the production of essential aromatic amino acids through competitive inhibition of the enzyme enolpyruvylshikimate phosphate (EPSP) synthase. This is a key enzyme in the shikimic acid pathway for the synthesis of chorismate which is a precursor for the essential aromatic amino acids phenylalanine, tyrosine and tryptophan. Thus, the efficacy of glyphosate is based on translocation to sensitive parts of plants and inhibition of the mode of action of key enzymes in the plant. Since the pathway is not present in animals, which instead obtain aromatic amino acids from their diet, animals are not affected by this function (Giesy et al. 2000; Monheit 2000).

Glyphosate translocation to and exudation from intact roots to soil is well known (e.g. Sprankle et al. 1975a; Schultz and Burnside 1980; Arnaud et al.1998; Geiger et al.

1999; Alister et al. 2004). Sprankle et al. (1975a) found that after foliage application the total translocation to rhizomes and shoots was 66.7 % of the foliage-adsorbed glyphosate, accounting for 35% of the total amount of glyphosate applied. In the studies of Schultz and Burnside (1980) and Alister et al. (2005), 52% and 22% of foliage-adsorbed glyphosate, respectively, were found in roots. Arnaud et al. (1998) reported that about 22% of applied glyphosate was recovered from roots.

In general, it has been stated that glyphosate does not degrade in glyphosate-sensitive plant cells or that the degradation is insignificant (e.g. Eberbach and Bowner 1995). However, according to Putnam (1976), a small amount of glyphosate was metabolized by apple and pear trees and, according to the FAO evaluation (1997), glyphosate is metabolized to aminomethylphosphonic acid (AMPA) in both genetically modified glyphosate-resistant and susceptible plants, but residues of AMPA in crops are usually low or undetectable, being higher in glyphosate-resistant crops.

1.3.4 Toxicity to terrestrial and aquatic animals

It is generally considered that glyphosate is largely non-toxic to terrestrial and aquatic animals, and that only very high doses can provoke toxic effects (Giesy et al. 2000; Monheit et al. 2004). However, Relyea (2005) showed that formulated glyphosate was very toxic to amphibians under natural conditions when sprayed with Roundup®, a leading commercial glyphosate product. This result, however, has been strongly criticised because of the atypical application rates, unrealistically high aqueous exposure and design limitations (Borggaard and Gimsing 2008).

Commercial herbicide products contain surfactants which are added to facilitate the penetration of the active ingredient through the cuticular waxes on target plants. In some cases the surfactants can contribute to the toxicity of herbicide formulations or the surfactants may be more toxic than the active ingredient. Roundup® contains polyethoxylate tallowamine (POEA) as a surfactant. It has been stated that the acute toxic effects on aquatic animals could be attributed to POEA and not the glyphosate (Giesy et al. 2000; Monheit 2004). In addition, Benachour and Séraline (2009) found serious damage in human cell cultures treated with Roundup or with POEA or AMPA alone. They concluded that "the proprietary formulations available on the market could cause cell damage and even death around residual levels to be expected, especially in food and feed derived from Roundup formulation-treated crops". However, it is difficult to estimate whether or not damage obtained in the cell cultivation would occur in human beings.

1.3.5 Glyphosate, AMPA and drinking water quality

According to the WHO statement (WHO, 2004), glyphosate and AMPA have similar toxicological profiles, and both are considered to exhibit low toxicity. Under usual conditions their presence in drinking water does not represent a hazard to human health. For this reason WHO has not established guideline values of drinking water quality for glyphosate and AMPA. On the contrary, the European Union (Directive 98/83/EC) retained the limit values for any individual pesticide and for total pesticides at 0.1μg L^{-1} and 0.5μg L^{-1}, respectively. However, these values are general limit values for pesticides and are not based on toxicological criteria.

1.3.6 Occurrence of glyphosate in watercourses

Based on its strong adsorption to soil, glyphosate is classified as an immobile compound. Nevertheless, glyphosate with its metabolite AMPA has been frequently detected in Norwegian, Swedish, Danish, Canadian and Dutch watercourse monitoring programmes (Ludvigsen and Lode 2001; Törnquist et al. 2002; Traas and Smit 2003; Scribner et al. 2003; Scribner et al. 2007; Adriaanse et al. 2008). The concentrations often exceeded the EU threshold value for drinking water (0.1 µg L^{-1}). In the US monitoring programme, AMPA was detected more frequently and occurred at similar or higher concentrations than glyphosate, and glyphosate and AMPA were detected more frequently in surface water than in groundwater (Scribner et al. 2007). Occasionally, glyphosate and AMPA were detected in surface and groundwater in Burgundy, France (Landry et al. 2005). In Finland, the monitoring of glyphosate and AMPA residues in river water was started in summer 2008. Residues were detected in two of eight analysed samples (1 July and 6 October). The concentrations were highest in October 2008 (0.22 µg L^{-1} for glyphosate and 0.46 µg L^{-1} for AMPA) (Siimes K., unpublished). In general, when glyphosate and AMPA residues were monitored, they were also frequently found.

According to Traas and Smit (2003), AMPA occurs widely in Dutch surface waters. Concentrations of up to 5.4ug L^{-1} were reported from monitoring networks. This clearly exceeds the European limit for drinking water, but the measured concentrations were below the Maximum Permissible Concentration for aquatic ecosystems (MPC_{water}) which is 79.7 µ L^{-1}. Traas and Smit (2003) pointed out that besides glyphosate, there are also other important parent compounds of AMPA, such as those phosphonates that are used as ingredients of detergents and coolants. Thus, part of the AMPA may originate from other chemicals than glyphosate.

1.3.7 Uptake of glyphosate residues by roots

The uptake of glyphosate residues by roots was documented by Sprankle et al. (1975b), Rodriques et al. (1982), Pline et al. (2002), Alister et al. (2005), Guldner et al. (2005) and Neumann et al. (2006). Released glyphosate can result in fairly high concentrations in the rhizosphere and can cause various negative effects in non-glyphosate-resistant plants through root uptake. Growth inhibition in adjacent plants and seedlings was reported by Rodriques et al. (1982), Pline et al. (2004), Guldner et al. (2005) and Neuman et al. (2006). Side-effects, such as inhibition of the acquisition of micronutrients (e.g. Cu, Mn, Zn, Fe and B) which are involved in the plant´s own disease resistance mechanisms, were reported by several scientists, e.g. Neumann et al. (2006).

1.4 Reactions of glyphosate in soil

1.4.1 Degradation and dissipation in soil

The degradation of glyphosate in soil is mainly a microbiological process. Torstensson (1985) concluded that the degradation rate of glyphosate correlates with the general microbial activity of the soil. The degradation times (DT50) of glyphosate can vary from a few days to several months and, in some cases, even years (Nomura and Hilton 1977; Carlisle and Trevors 1988). The main metabolite is AMPA (aminomethylphosphonic acid), accounting for more than 90% of metabolites. Sarcosine is another metabolite, accounting for about 3% of metabolites. Biodegradation is influenced by adsorption/desorption, but also by the edaphic and climatic conditions which control the activity of the microflora. For instance, Gimsing et al. (2004) showed that the mineralization rate of glyphosate correlates best with the numbers of *Pseudomonas* spp. bacteria, and that phosphate addition stimulates mineralization in soils with a low mineralization rate. According to e.g. Heinonen-Tanski (1989) and Stenrød (2005), temperature is an important factor determining the degradation of glyphosate.

As previously reviewed, glyphosate is considered to be strongly sorbed on soil particles and therefore supposed to be almost immobile with a low tendency for transport in the soil matrix or leaching from the soil surface. Moreover, glyphosate is often considered to be easily biodegradable in soil, and this as well would decrease the leaching risk.

But are those two assumptions true in all cases? Recently, there was a discussion about the fate of bound and aged residues in soil (Gevao et al. 2000; Barraclough et al. 2005; Mamy and Barriuso 2007). The initial sorption of pesticides can, anyhow, become less or non-reversible with time, with the formation of bound or aged residues by some chemicals and some soils. In the case of strongly sorbed chemicals, these fractions can increase when the contact time between chemicals and soil increases. Time-dependent sorption of glyphosate was reported also by Heinonen-Tanski (1989) and Nomura and Hilton (1997).

Only few studies have been published concerning the behavior of AMPA in soil. Scribner et al. (2007) reported that trace levels of glyphosate and AMPA may persist in the soil from year to year, and Simonsen et al. (2008) found residues of glyphosate and AMPA in soil sprayed over two years earlier. However, it has been concluded that AMPA degrades at a slower rate than glyphosate (Rueppel et al. 1977; Giesy et al. 2000; Mamy and Barriuso 2005). Formsgaard et al. (2003) detected background concentrations of AMPA, but not of glyphosate, in soil from fields sprayed three and five years earlier. These results suggest that formation of aged residues (both glyphosate and AMPA) may occur in different soils and under different circumstances.

The results of an outdoor lysimeter study (Al-Rajab et al. 2008) showed that nearly 70% of the initial glyphosate was present in the soil in a form non-extractable by 0.1 M KH_2PO_4 (a very weak extractant) at the beginning of the experiment, and less than 20% of the residues were present in the soil after 11 months. Contamination of water with glyphosate residues continued for a period of more than one year. These findings suggest that glyphosate largely adsorbs to soil and that non-extractable residues may become available and take part in biodegradation and leaching. Simonsen et al. (2008) noticed that also aged residues are bioavailable.

1.5 Adsorption and desorption

After spraying glyphosate will be strongly sorbed to soil (e.g. Piccolo and Celano 1994; Tiberg 1998; de Jonge and de Jonge 1999; Gimsing and Borggaard 2001; Mamy and Barriuso 2005), which thus restricts its mobility. Glyphosate sorption is considered to be time-dependent. Rapid initial equilibrium adsorption is followed by a slower time-dependent sorption.

Because glyphosate is a polyprotic acid with three polar functional groups (carboxyl, amino and phosphonate groups; Table 1.1.), with an active phosphanate end-group to the molecule, glyphosate is able to form inner-sphere complexes on the Al and Fe oxide surfaces in soil (e.g. Sheals et al. 2002; Gimsing and Borggaard 2002). This means that glyphosate reacts with the same soil components as phosphates (Gerritse et al. 1996; Gimsing and Borggaard 2001; Wang et al. 2005) and competes with phosphate for the same sorption sites.

Sorption on the same soil constituents suggests that added and adsorbed phosphate may affect the retention, degradation and leaching of glyphosate. Sprankle et al. (1975b) were the first to produce evidence that phosphate can diminish glyphosate adsorption. This finding was confirmed in later studies (e.g. Hance 1976; de Jonge and de Jonge 1999; de Jonge et al. 2001; Dion et al. 2001; Gimsing and Borggaard 2001 and 2002; Wang et al. 2005), and phosphate is considered to be a stronger competitor for sorption sites than glyphosate. However, Gimsing et al. (2004) noticed that also glyphosate is able to displace phosphate to some extent. This was also noticed by Barret and McBride (2007) who added that the ability of glyphosate to compete with phosphate is limited and displacement of adsorbed phosphate by glyphosate requires glyphosate application in much higher than normal agronomic rates.

1.6 Assessment of environmental fate of gyphosate

As discussed above, the Freundlich sorption coefficient (K_F) is used in the risk assessment. However, it is likely that the K_F coefficient alone does not adequately describe the movement risk within a given soil profile, even in soil with homogeneous texture. For instance, glyphosate may be transported via roots to deeper soil horizons that differ in their chemical properties from the upper soil layer. Walls of root channels can enrich with glyphosate released from dead root material. As part of soil macropore network, root channels serve as transport routes for solutes and small particles through the soil.

According to the reviews of Vereecken (2005) and of Borggaard and Gimsing (2008), soil P status, the amount of metal oxides and in some cases soil pH are factors controlling glyphosate adsorption. Of these factors, soil P status is an accessible and thus attractive option to be utilized in the assessment of environmental risk. Although it has been stated that the leaching risk of glyphosate might be greater in phosphorus-rich soils, the question "how rich" was not answered. In spite of doubt about its suitability for risk assessment (e.g. de Jonge et al. 2001; Borggaard and Gimsing 2008), it is worth testing whether soil phosphorus status could be used for this purpose. The Agri-Environmental Programme in Finland requires the P status of fields to be determined at regular intervals. Thus, a large amount of data on P_{AC} concentrations exists at farm level.

Knowledge about glyphosate persistence and losses to overland flow on a field-scale is scarce. Application time and other cultivation practices and climatic factors affect the behaviour of pesticides impeding application of laboratory tests to outdoor conditions. Thus, a field-scale experiment is needed to compare the results of laboratory studies and real-world practice.

The efficacy of glyphosate as a systemic broad-spectrum herbicide is based on its translocation to sensitive parts of the plant and inhibition of the mode of action of key enzymes in the plant. Only effective translocation of glyphosate in plants gives good control of glyphosate-sensitive weeds. As reviewed in Section 1.3.3, the proportion of glyphosate translocated to roots can even exceed 20% of the applied amount. This raises the question of whether translocation does constitute a significant source of glyphosate residues in soil. There are no previous studies concerning this possibility.

1.7 Aims of the study

The main aim of this thesis was to form a holistic view of the major factors influencing the behaviour of glyphosate in Finnish agricultural soil, and to find practical indicators for assessing its accumulation and leaching risk.

To achieve the main goal, five separate experiments were established. The more detailed objectives of the individual studies were:

1. To compare the adsorption of glyphosate to three conventional sugar beet herbicides on different soils and to get data for assessment of the leaching risk.

2. To compare the persistence and transport in soil of the five herbicides studied in sugar beet cultivation, and to produce a data set for model calibration and environmental risk assessment.

3. To determine whether it is possible to assess the accumulation tendency and leaching risk of glyphosate on the basis of data on P status. The study was undertaken to compare the retention tendency of glyphosate and its dependency on the P status of soils.

4. To examine the behaviour and persistence of glyphosate in soil and the magnitude of its losses in leaching waters on a field scale in a northern climate. Attention was also paid to the relationship of the glyphosate losses to the losses of phosphorus.

5. To clarify the significance of glyphosate translocation via plants to glyphosate residues in soil, and to discuss the significance of this transport mechanism on a field scale.

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CHAPTER 3

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CHAPTER 4

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CHAPTER 5

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CHAPTER 6

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