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

Doctoral Dissertation

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MTT

MTT SCIENCE 3

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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.

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.

ACKNOWLEDGEMENTS

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

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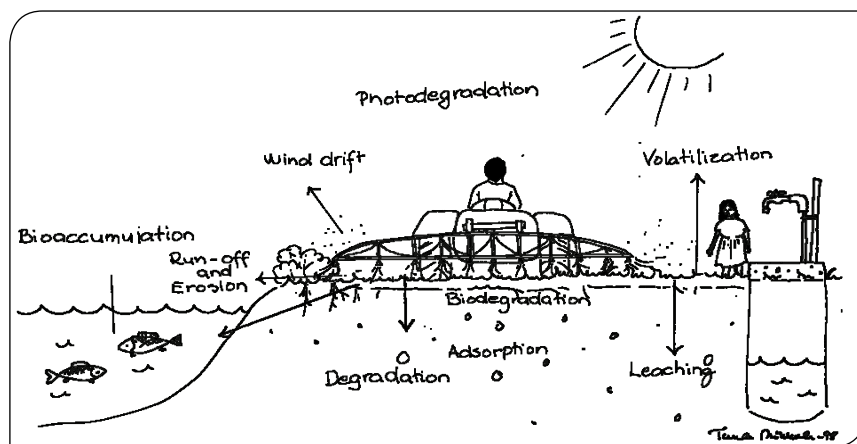
Figure 1.1. Environmental fate of pesticides. (Drawing of Tiina Mikkola 1998).

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:
$$S = K_d C \qquad \text{(Equation 1)}$$

Freundlich sorption isotherm:
$$S = K_F C^{1/n} \qquad \text{(Equation 2)}$$

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.

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

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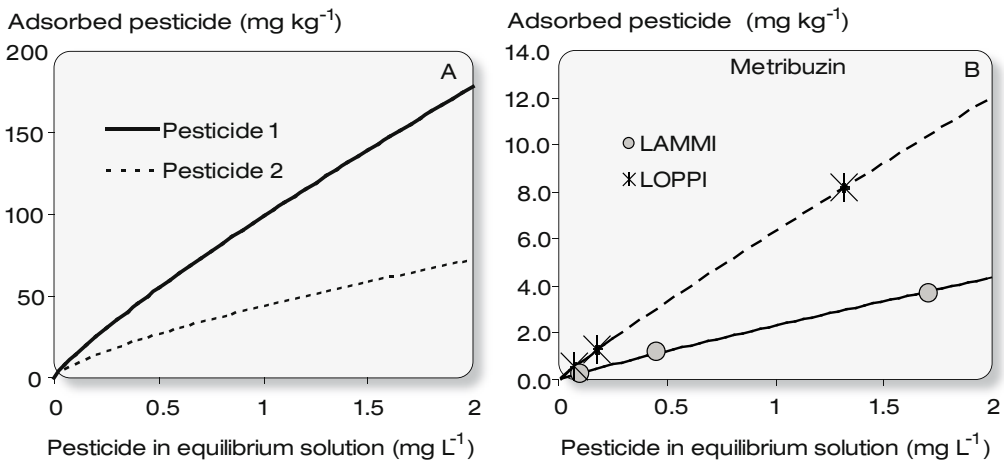
Figure 1.2. Adsorption isotherms for two different pesticides (A) in the same soil and metribuzin in two different soils (B). The Lammi soil was sandy and the Loppi soil sandy loam with high organic carbon content. (Figure B: Rämö (2008). Published by permission of MTT Agrifood Research Finland).

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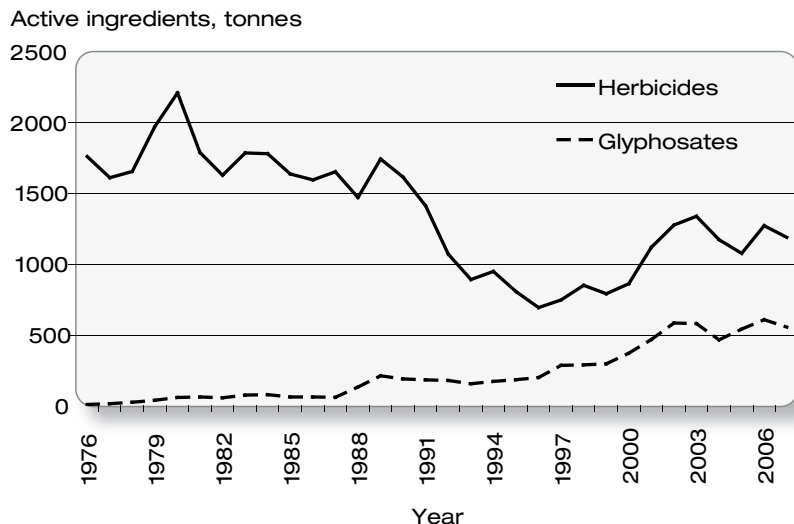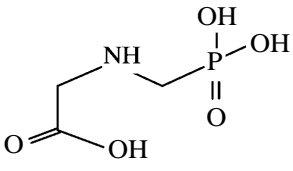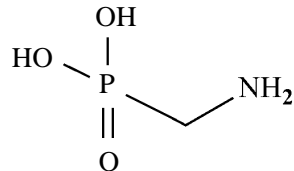
Figure 1.3. Sales of herbicides and glyphosates in 1976-2008 in Finland (tonnes of active ingredients). Savela 2009. Personal communication. (Published by permission of Evira.).

Parameter	Glyphosate[a]	AMPA[b]
Chemical structure	(structure of glyphosate: NH, P with OH, OH, O; and O=C–OH)	(structure of AMPA: HO, P with OH, O, NH₂)
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	7.5×10^{-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^{-1c}	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 endgroup 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 2
Adsorption of sugar beet herbicides to Finnish soils

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CHAPTER 3
Soil phosphorus status in environmental risk assessment for glyphosate and glufosinate-ammonium

Laitinen, P., Siimes, K., Rämö, S., Jauhiainen, L., Oinonen, S., Eronen, L. & Hartikainen, H. (2008).

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CHAPTER 4
Fate of the herbicides glyphosate, glufosinate-ammonium, phenmedipham, ethofumesate and metamitron in two Finnish arable soils

Laitinen, P. Siimes, K., Eronen, L., Rämö, S., Welling, L., Oinonen, S, Mattsoff, L. & Ruohonen-Lehto, M. (2006).

CHAPTER 5
Glyphosate and phosphorus leaching and residues in boreal sandy soil

CHAPTER 6
Glyphosate translocation from plants to soil – does this constitute a significant proportion of residues in soil

CHAPTER 7
General discussion

General discussion

General discussion about the fate of glyphosate in agricultural soil

Soil chemical and physical properties together with climatic conditions are considered to determine the fate of glyphosate in soil. The aim of the current thesis was to study glyphosate sorption in different soils (Chapter 2), the effect of the soil phosphorus status on glyphosate sorption and desorption (Chapter 3), the persistence and movement of glyphosate in the soil profile under field conditions (Chapters 4 and 5) and the translocation of glyphosate from plants to soil (Chapter 6). The experimental schedule is given in Table 7.1.

Table 7.1. Experimental schedule of the glyphosate (GLY) studies. PAC is acid ammonium acetate-extractable phosphorus, and DPS is the degree of phosphorus saturation.

	Test	Years	Soil in Table 7.2	Janakkala Sandy loam	Perniö Clay	Toholampi Sandy silt loam	Chapter
Adsorption tests:							
- adsorption in 21 soils	TEST I	1999	2 - 21	9 -10	7 - 8	17 - 19	2
- GLY adsorption/soil P_{AC}	TEST II	1999-2000	7 and 9	x	x		3
- GLY desorption/soil P_{AC}	TEST III	2001	7 and 9	x	x		3
- GLY adsorption/soil P_{AC}/ DPS	TEST IV						
Field experiment:							
- sugar beet cultivation		1999-2001	7 - 10	x	x		4
- leaching field		2001-2003	17 - 19			x	5
Pot experiment:							
- translocation from plants		2002	17			x	6

7.1 Glyphosate sorption to soil

Strong sorption on soil particles is known to retard degradation and to cause accumulation of chemicals in the soil. Thus, the prolonged or repeated use of herbicides, especially those with strong sorption and slow degradation, may lead to their accumulation. Transport of strongly sorbed compounds from field to aquatic environment can occur as solutes or bonded to soil colloids, as has been shown by Vereecken (2005) for glyphosate and by Laubel et al. (1999) and Turtola (1999) for phosphorus. Both forms can be transported in the soil by surface runoff and subsurface flow, thus resulting in a risk of water pollution (Borggaard and Gimsing 2008).

Sorption experiments (Chapters 2 and 3) were carried out according the standard batch equilibration method (OECD Guideline 106, 1982) using unlabelled glyphosate. The method was described in Chapters 2 and 3. The recovery of glyphosate in the analyses was 88 to 104% of the added amount.

In Chapter 2, the adsorption of glyphosate was studied in 20 soil samples collected from 12 different sites in plough and subsoil layers (TEST I). The soil properties and the K_F values obtained are presented in Table 7.2. The higher the K_F value, the stronger the sorption in soil. Great variation of the K_F values (from 37 to 303) between different soils was observed.

The correlation between glyphosate K_F values and soil properties, such as organic carbon content, texture, pH and soil phosphorus status [acid ammonium acetate (P_{AC})], was tested (see Chapter 2, Figures 2 and 3). None of the soil properties alone explained the variation in sorption, presumably owing to the physical and chemical heterogeneity of the soil in the sampled layers. Very similar variation has been reported in the literature. In the study of Glass (1987), the K_F value was 33 for sandy loam, 56 for silt loam and 76 for clay loam soils, in that of Piccolo et al. (1994) it varied from

Table 7.2. Glyphosate K_F, 1/n and K_{FOC} values, mobility classes and soil properties. K_F values were used to predict glyphosate mobility. NA=not analysed.

Soil	Site	Soil type	Depth	Glyphosate				pH	OC	Clay	Silt	P_{AC}[a]
			cm	K_F	1/n	Mobility[b]	K_{FOC}	CaCl$_2$	%	%	%	mg L^{-1}
1	Kokemäki	silty loam	0-20	NA	NA		NA	5.4	2.42	17	62	10.7
2			20-40	166	0.97	immobile	34926	6.1	0.47	17	66	1.6
3	Kotkanoja	clay	0-20	55	0.92	slightly mobile	1914	5.8	2.88	46	15	3.0
4			20-40	249	0.91	immobile	46436	5.6	0.54	58	13	1.1
5	Rehtijärvi	sandy loam	0-20	44	0.9	slightly mobile	6039	5.8	2.57	13	8	27.4
6			20-40	55	1	slightly mobile	2139	5.7	0.72	4	3	17.1
7	Perniö[cd]	clay	0-30	97	1.03	immobile	1374	6	7.06	41	24	4.1
8			30-60	41	1.02	slightly mobile	1370	6	2.96	47	28	1.5
9	Janakkala[cd]	sandy loam	0-30	97	0.85	immobile	1643	6.4	5.93	4	15	3.3
10			30-60	51	0.86	slightly mobile	2900	5.9	1.77	4	13	0.9
11	Perniö	clay	0-25	58	0.93	slightly mobile	2193	8.1	2.67	41	43	38.7
12		clay	25-50	113	0.87	immobile	4500	7.9	2.5	(>30%)	26	22.4
13	Turenki	sandy loam	0-20	93	0.9	immobile	3946	7.1	2.35	12	NA	8.8
14			20-45	90	0.86	immobile	11986	6.8	0.75	8	NA	2.8
15	Perniö	clay	0-30	179	1.26	immobile	2544	6	7.05	41	24	5.8
16	Turenki	sandy loam	0-30	121	0.98	immobile	2045	6.3	5.93	4	15	6.4
17	Toholampi[e]	sandy silt loam	0-25	159	0.93	immobile	2014	6.2	7.9	5	16	10.0
18			25-35	102	1.05	immobile	2273	5.6	4.5	4	20	3.6
19			35-60	37	0.76	slightly mobile	2823	5.1	1.3	8	30	3.5
20	Jokioinen	muddy clay	0-30	84	0.91	slightly mobile	664	6.9	12.6	57	NA	52.0
21	Jokioinen	organic soil	0-30	303	1.14	immobile	1165	5.2	26	79	13	5.1
	Mean			110	0.95		6745	6.2	4.9	25.9	21.9	11.0
	SD			70.88	0.111		12008	0.8	5.9	23.9	14.8	14.0

[a]Readily extractable phoshorus, detemined as P dissolved in acid ammonium acetate in pH 4.65.

[b]Based on the Finnish mobility limits.

[cd]Used also in the P status tests and in the field studies.

[e]Used also in the leaching field study.

13.8 to 152.9 for sandy and silty soils and in a study of Al-Rajab (2008) from 16.6 for clay loam soil to 33.6 for silt clay loam soil and 34.5 for sandy loam soil. Comparable results were also presented by Tiberg (1998) in 13 Nordic reference soils.

Interestingly, at most sampling sites the sorption in the plough layer was clearly different from that in the deeper layers where it was either higher or lower (Table 7.2). This means that the mobility of glyphosate may vary layer by layer, which should be taken into account when predicting the leaching risk through the soil matrix. For instance, in Perniö (clay, soils 11 and 12) the adsorption was weaker in the plough layer (K_F 58) than in the subsoil (K_F 173). On the contrary, in Toholampi (sandy silt loam, soils 17-19) the sorption was stronger in the plough layer (K_F 159) than in the subsoils (K_F 102 and 37). Thus, according to the K_F determinations, glyphosate was slightly mobile in the plough layer and immobile in the subsoil in Perniö, whereas in Toholampi it was more mobile in the subsoil than in the plough layer.

Glyphosate can compete with phosphate for the same sorption sites, and phosphate may displace sorbed glyphosate (Sprankle et al. 1975a; de Jonge et al. 2001; Gimsing and Borggaard 2001; Gimsing and Borggaard 2002). Peltovuori (2006) demonstrated that in Finnish mineral soils the phosphorus sorption capacity typically decreases with increasing depth. In the study on the Kotkanoja field (clay soil), he found that the plough layer (0-24 cm) with the highest Al and Fe oxide concentrations had the greatest theoretical evaluated phosphorus sorption capacity (EPS). In the Toholampi field, on the contrary, EPS and oxide fractions were largest at the depth of 27-39 cm. In both soils, the degree of phosphorus saturation (DPS) was higher in the plough layer than in the deeper ones. These outcomes suggest that in Kotkanoja the plough layer is lower at sorption sites available also for glyphosate, and

the K_F value is lower than in the deeper layers, whereas in Toholampi the K_F value is lower in the subsoil. In our study this suggestion was confirmed in the Kotkanoja soil but not in the Toholampi soil (Table 7.2). The conflicting results obtained for Kotkanoja and Toholampi soils can be attributed to the differences in soil properties and to some differences in possible reaction mechanisms. Glyphosate is able to be bound by soil components through its several functional groups (Table 1.1). In contrast to phosphate, on oxide surfaces glyphosate may even form a tetradentate bond as shown in Figure 7.1

7.1.1 Effects of soil phosphorus status on glyphosate sorption

In Chapter 3, the relationship between soil phosphorus status and adsorption of glyphosate was investigated to determine whether acid ammonium-extractable phosphorus (P_{AC}) could be utilised in the assessment of glyphosate mobility. The adsorption of glyphosate (TEST II) was studied in clay and sandy loam soils (soils 7 and 9, Table 7.2) enriched with increasing amounts of P added as KH_2PO_4. Desorption of glyphosate (TEST III) was determined for some P-enriched soil samples
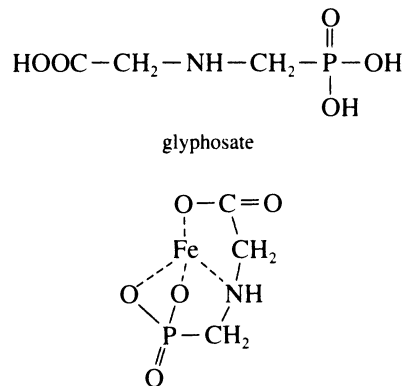

Figure 7.1. Glyphosate structure and its bonding on Fe oxide surface. (According to M.B. McBride 1994. Environmental Chemistry of Soil p. 371).

Furthermore, an additional test was done to determine the relationship between glyphosate adsorption and the degree of phosphorus saturation (DPS) of the soil (TEST IV).

For the two individual soils, adsorption of glyphosate decreased with increasing P_{AC} value (TEST II). The negative correlation between K_F and P_{AC} was non-linear but high ($r > -0.98$) in both soils. The K_F value decreased with increasing P_{AC} value more drastically in sandy loam than in clay soil. This difference between the soils can be explained by their dissimilar sorption capacity. More phosphate was required to raise the P_{AC} values to the same level in the sandy loam soil than in the clay soil. This finding is consistent with the higher Fe and Al oxide concentration of the sandy loam (in total 261 mmol kg^{-1} in sandy loam and 216 mmol kg^{-1} in clay) and their lower phosphorus saturation. This means that after the same P addition there were still more sorption sites available for glyphosate in the sandy loam soil than in the clay soil. This is consistent with earlier studies and, according to the review

by Vereecken (2005), soil P status and the amount of iron and aluminium oxides are major factors controlling the adsorption of glyphosate.

In order to clarify the relationship of glyphosate adsorption to soil P bound by Al and Fe oxides (TEST IV), P was fractioned by oxalate-extraction according to a modified Chang and Jackson method (Hartikainen, 1979) where P_{NH4F} is assumed to be bound by Al oxides and P_{NaOH} by Fe oxides. DPS was then calculated as a molar ratio of ($P_{NH4F}+P_{NaOH}/$ [$0.5*(Al_{OX}+Fe_{OX})$]). The results of the test are presented in Table 7.3.

As expected, the P concentration was related to the oxide concentration and P saturation. The DPS rose more slowly in the sandy loam soil where the oxide concentration was higher. Sorption of the added P to both Al and Fe oxides was similar in clay soil, whereas in sandy loam more phosphorus was sorbed by Al oxides than by Fe oxides. This is also analogous to the oxide concentrations; in clay the concentrations were quite similar, whereas in the

Table 7.3. Freundlich adsorption coefficient (K_F) and degree of phosphorus saturation (DPS) for glyphosate at different levels of phosphorus status (P_{AC}) in the plough layer. The amount of Al oxides was 84 mmol kg^{-1} for clay and 186 mmol kg^{-1} for sandy loam and the amount of Fe oxides was 132 mmol kg^{-1} and 76 mmol kg^{-1}, respectively.

	Added P	P_{AC}	K_F	P_{NH4F}[a]		P_{NaOH}[a]		P_{TOT}[b]	DPS[c]
	mg kg^{-1}	mg L^{-1}	L kg^{-1}	mg kg^{-1}	mmol kg^{-1}	mg kg^{-1}	mmol kg^{-1}	mmol kg^{-1}	%
Perniö (clay)	0	4.1	98.7	47.5	1.5	160.3	5.2	6.7	6.2
	100	8.6	68.1	109.8	3.5	252.2	8.1	11.7	10.8
	300	16.1	71.2	116.0	3.7	261.9	8.5	12.2	11.3
	600	31.9	48.1	195.0	6.3	318.1	10.3	16.6	15.3
Janakkala (sandy loam)	0	3.3	98.9	191.3	6.2	112.8	3.6	9.8	7.5
	200	8.9	87.9	246.8	8.0	135.0	4.4	12.3	9.4
	500	15.0	61.8	324.3	10.5	146.6	4.7	15.2	11.6
	900	26.6	48.9	456.0	14.7	183.8	5.9	20.7	15.8

[a]Inorganic P fractions: P_{NH4F} is assumed to be bound by Al oxides and P_{NaOH} by Fe oxides.
[b]Sum of P bounded by Al and Fe oxides.
[c]Degree of P saturation. Calculated as a molar ratio of ($P_{NH4F} +P_{NaOH}$) /[$0.5*(Al_{OX} + Fe_{OX})$].

sandy loam there was a greater amount of free Al oxides than Fe oxides.

The concentration of soil oxides and their P saturation was reflected in the added amounts of phosphorus and glyphosate sorption; with increasing DPS, adsorption of glyphosate decreased (K_F values decreased) (Table 7.3). DPS_{Ox}, based on oxalate extraction, has earlier been used as an indicator of P leaching. According to Van der Zee et al. (1987), the critical DPS_{Ox} value for substantial P movement in surface and subsurface water is 25% and, according to Holford et al. (1997), phosphorus leaching began when 17–38% of the sorption capacity of soil horizons was saturated. However, these DPS values cannot directly be applied to Finnish soils rich in apatitic phosphorus dissolving in oxalate extraction, thus leading to highly overestimated values. On the other hand, Uusitalo and Aura (2005) demonstrated that phosphorus losses increase when soil P_{AC} increases and they also found an exponential relation between P_{AC} and P saturation by Mehlich 3 extraction (DPS_{M3}) (Mehlich 1984).

A comparison of our simultaneous DPS, P_{AC} and K_F values with the Finnish mobility classes (Chapter 3, Table 7) suggests that the mobility of glyphosate increased from immobile to slightly mobile at DPS values >9 and from slightly mobile to slowly mobile when the DPS was >16% in the sandy loam. Although the available data is small, it can be considered as a preliminary test of the possibility of using P_{AC} data for environmental risk assessment. The potential of P_{AC} and DPS as indicators of the glyphosate leaching risk is worth further studies.

7.1.2. Effect of soil phosphorus status on reversibility of glyphosate adsorption

The reversibility of glyphosate adsorption was tested in the desorption test with a sandy loam soil at three phosphorus lev-els (6.4, 26.8 and 89.0 mg P_{AC} L^{-1}), and in a clay soil at one phosphorus level (5.8 mg L^{-1} P_{AC}) (TEST III). The results of the sandy loam soil tests (see Chapter 3, Table 3 and Figure 3) showed a decrease in glyphosate sorption when soil test P (P_{AC}) concentration increased. Sorption equalled 95% of the applied glyphosate for the subsample with low soil adsorption test P level (5.8 mg P_{AC} L^{-1}) and 84% for the highest soil P status (89 mg) mg P_{AC} L^{-1}. The consequent desorption of sorbed glyphosate was 6% for the low soil test P and 13% of the initially adsorbed amount (Chapter 3, Figure 3). This means that in total the amount of dissolved glyphosate was 11% for the lowest and 27% for the highest P_{AC} level. In other words, the amount of mobile and potentially leachable glyphosate increases drastically at an excessive phosphorus level. As concluded earlier by de Jonge et al. (2001), Dion et al. (2001), Gimsing et al. (2004a) and Mamy and Barriuso (2005), this is due to the competition of phosphate for sorption sites, which weakens the glyphosate binding strength and renders the adsorption more reversible. According to Al-Rajab et al. (2008), desorption was about 6.7 and 23% of the initially sorbed glyphosate, being highest for clay loam which had the highest phosphorus status. However, they concluded that the most important factor controlling the fate of glyphosate in the soil was soil pH.

7.1.3 Developing and fitting a statistical model

Using the data of the adsorption test (see Chapter 3, Table 3 and Table 7.2), statistical models of the relationship between the soil P_{AC} values and the glyphosate adsorption coefficient (K_F) were developed and fitted. The relationship was not linear and for low P_{AC} vales, a simple exponential model did not give a good fit either. Therefore, a double exponential model was fitted. This model, with slightly different parameter values, was suitable for both soils (Chapter 3, Table 5 and Figure 4).

The model was tested with the independent data set presented in Chapter 3, Table 6. The same data is presented in this chapter in Table 7.2. The model fitted the data set well only when the soil P status was good or high (P_{AC} from 14 to 40), and it underestimated the sorption when the P status was very low and the determined K_F value was simultaneously very high (>120) (Chapter 3, Table 6). Anyway, such high K_F values indicate very strong adsorption and accumulation risks in the soil. Our independent data set did not include excessive P_{AC} values where the adsorption coefficients could have been lower than obtained in the test with phosphorus-manipulated soils (TEST II). The equations may be a useful tool in assessing the leaching risks of glyphosate when P_{AC} was at good and high levels, but it is obvious that the equations are not useful for all soil types (e.g. soils with high organic carbon content).

Validation of the model was difficult, because the available data was small and heterogeneous. The relationship between soil test P and the coefficient K_F of the glyphosate sorption equation is clear when manipulating P_{AC} of a single soil. However, this relationship is blurred (Figure 7.2) when a heterogeneous set of soils is studied and other variables cannot be fixed. Thus, the model must be calibrated in those cases where enough data is available.

Because K_F values are used for the classification of pesticide mobility and leaching risks, we compared our results with the Finnish mobility limits of pesticides (Nikunen et al. 2000). The exponential models (see Chapter 3, Equations 4 and 5) were used to calculate the P_{AC} values corresponding to the mobility limit classes (see Chapter 3, Table 7). The mobility of glyphosate varied from immobile to low, being slight when the P status was at the level typical of Finnish soils, in the range of 3-30 mg L^{-1} according to Mäntylahti (2003).
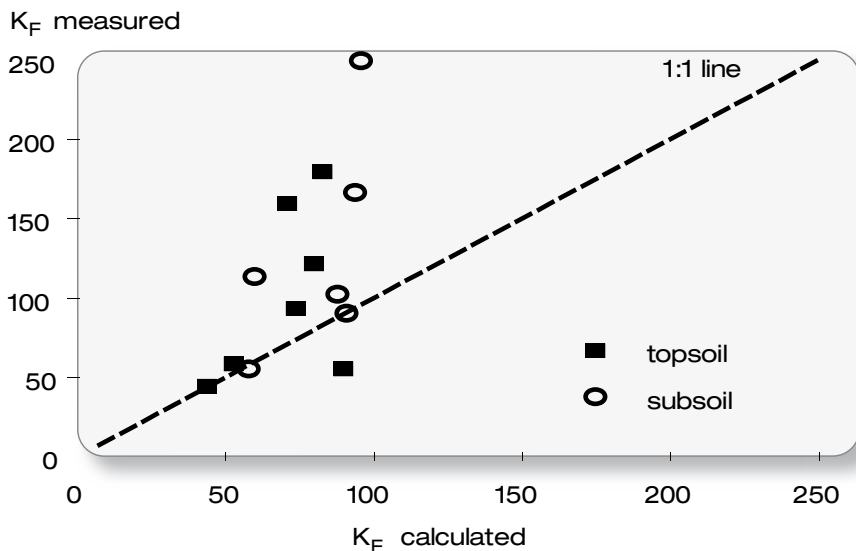
Figure 7.2. Calculated and measured sorption coefficient values KF for glyphosate.

7.2 Behaviour of glyphosate in the field studies

According to the prevailing concept, aged chemicals are less available for uptake by micro-organisms and hence for microbial degradation (Alexander 2000). However, Simonsen et al. (2008) showed that six–month-old residues of glyphosate and AMPA were still bioavailable. In our study, the movement and field dissipation of glyphosate were monitored in two field trials with sugar beet, and in a leaching field trial with cereals (Table 7.1). The objectives were to compare the persistence and transport of five herbicides and to compile a data set for environmental risk assessment (Chapter 4). Since the study lasted two years, it was also possible to assess the herbicide accumulation risk. In the leaching field study the behaviour and persistence of glyphosate in soil and the losses in leachate waters on a field scale were studied (Chapter 5). The relationship between losses of glyphosate and phosphorus by surface runoff water was also examined.

Residues of glyphosate and AMPA were analysed 1-6 months after sampling. A high-performance liquid chromatograph (HPLC) and fluorescence detector were used for compound separation and identification. A Pickering Laboratories PCX 5100 post-column reaction module was used for derivatisation of glyphosate and AMPA. The chemicals and instruments used have been described in Chapters 4 and 6. Recoveries for analyses are given in Table 7.4. The results of residue analysis were not corrected with recoveries. The method used for glyphosate recoveries was described by Spann and Hargreaves (1994). The authors obtained recovery as high as 79-93% for Australian soils. Our results were lower but, as has been stat-

Table 7.4. Glyphosate and AMPA recovery efficiencies (RSD) for soil, root and water samples. NA = not analysed.

Site and soil	Recovery efficiency % and (RSD %)			
	Sample	Glyphosate	AMPA	Chapter
	Soil (depth cm)			
Janakkala (sandy loam):	0-28	41 ± 3^a	53 ± 6^a	4
	0-28	35 ± 8^b	46 ± 9^b	4
	28-50	41 ± 5^b	58 ± 1^b	4
Perniö (clay):	0-28	31 ± 6^a	39 ± 9^a	4
	0-28	40 ± 9^b	54 ± 7^b	4
	28-50	59 ± 5^b	75 ± 7^c	4
Toholampi (sandy silt loam):	0-25	45 ± 14^b	62 ± 13^b	5 and 6
	0-35	NA	NA	5
	35-60	47 ± 4^b	74 ± 11^b	5
	Roots	114 ± 3	70 ± 3	5 and 6
	Distilled water	63 ± 13	77 ± 9	5
	Leachate water	92 ± 12	98 ± 10	5

[a]Chapter 5: Figure 5, extraction procedure A.
[b]Chapter 5: Figure 5 extraction procedure C.

ed by Stalikas and Konidari (2001), low glyphosate recoveries are often associated with high adsorption to soil.

7.2.1 Cultivation practices

The sugar beet experiment was conducted in Janakkala and Perniö, Southern Finland, in 1999-2001 (Chapter 4). These study sites were selected on the basis of their P status and soil texture, the soil types being sandy loam (Janakkala) and clay (Perniö).

Apart from P_{AC} status, the study sites represented typical sugar beet fields in their texture and drainage systems. The same soils were used as testing materials when the impact of soil phosphorus status on glyphosate sorption was examined (Chapter 3), thus these soils with low phosphorus status were selected. In Janakkala and Perniö fields, two or three glyphosate applications were done in June and July, and the soils were tilled in autumn and/or spring (Table 7.5).

Table 7.5. Cultivation practices and glyphosate applications in the Janakkala, Perniö and Toholampi experimental fields. Previous glyphosate treatments are also given. Application rates are given as active ingredient.

	Janakkala (Sandy loam)	Perniö (Clay)
Glyphosate application	Autunm 1998	Autumn 1997
Ploughing (20 cm)	27.04.1999	Autumn 1998
Harrowing and sowing sugar beet	12.05.1999	13.05.1999
Glyphosate application (720 g ha^{-1})	10.06.1999	11.06.1999
Glyphosate application (720 g ha^{-1})	01.07.1999	01.07.1999
Harvesting	17.10.1999	18.10.1999
Ploughing (20 cm)	27.04.2000	Autumn 1999
Harrowing and sowing sugar beet	09.05.2000	05.05.2000
Glyphosate application (720 g ha^{-1})	06.06.2000	06.06.2000
Glyphosate application (720 g ha^{-1})	27.06.2000	27.06.2000
Glyphosate application (720 g ha^{-1})	11.07.2000	12.07.2000
Harvesting	14.09.2000	13.09.2000
	Toholampi (Sandy silt loam)	
Glyphosate application	Autumn 1989	
Ploughing (25 cm) and harrowing (5 cm)	Autumn 2000	
Sowing (barley)	01.06.2001	
Harvesting	02.09.2001	
Glyphosate application (1000 g ha^{-1})	17.09.2001	
Ploughing (0-25 cm)	22.05.2002	
Harrowing and sowing barley	25.05.2002	
Harvesting	13.08.2002	
Ploughing (25 cm) and harrowing (5 cm)	23.08 2002	
Sowing rye	24.08.2002	

The leaching study was carried out in 2001-2003 in Toholampi, Western Finland (Chapter 5). The soil type was sandy silt loam, only one glyphosate application was done in the autumn 2001 and the soil was ploughed in the next spring (Table 7.5). Hereafter the study sites are referred to as Janakkala (sandy loam), Perniö (clay) and Toholampi (sandy silt loam). A commercial glyphosate product, Roundup Ready®, was used in the Janakkala and Perniö fields, and Roundup® in the Toholampi field.

7.2.2 Sorption of glyphosate within the soil profiles of the test fields

According to the sorption tests, glyphosate was adsorbed more strongly on the topsoil of the Toholampi silt loam than on the topsoils of the other sites; the K_F values were 159.0 for the Toholampi soil, 97.0 for the Janakkala soil and 97.0 for the Perniö soil (Table 7.2, soils 17, 9 and 7, respectively). The adsorption (as percentage of added chemical) amounted in the plough layer to about 96% for Janakkala, 94% for Perniö and 97% for Toholampi. In the deeper layers it was 5 to 11% lower than in the topsoils. Desorption of the adsorbed glyphosate was only 5-7% in Perniö (clay) and Janakkala (sandy loam) (Chapter 3, Figure 3). For the Toholampi soil, desorption was not measured. The strong adsorption and limited desorption indicate that glyphosate is relatively persistent and its mobility in the soil matrix is low. According to the Finnish mobility limits (Nikunen et al. 2000), glyphosate was immobile at all study sites (K_F value >75).

7.2.3 Background residues

At the beginning of the research, background residues of glyphosate or AMPA were found in the plough layer at all study sites (Table 7.6). At the Janakkala sandy loam site, glyphosate had been applied in the previous autumn (1998) and in the following May, about 33% of the applied dose was still detected as glyphosate and 44% as AMPA (Table 7.6). In the Perniö clay soil, glyphosate had been used 18 months prior to the present study, probably even before that. No background glyphosate was detected, but the AMPA residue corresponded to 27% of the glyphosate used in the latest known applications. It has to be pointed out that the limits of quantification for glyphosate (0.02-0.05 mg kg^{-1}) and AMPA (0.02 mg kg^{-1}) correspond to residues of about 10 and 6%, respectively, of the amount applied in a single application of glyphosate in the plough layer (Chapter 4). This means that here may be significant bound residue concentrations in the soil that cannot be quantified.

Table 7.6. Glyphosate and AMPA residues in soil [(mg kg^{-1} in dry soil) and proportion (%) of applied glyphosate] in plough layers in spring after autumn application.

Site	Application	Time	GLY	GLY	AMPA	AMPA	Total
	g ha^{-1}	months[a]	mg kg^{-1}	%	mg kg^{-1}	%	%
Janakkala (sandy loam)[b]	1440	8	0.14	33.4	0.12	44	77
Perniö (clay)[b]	1440	18	<0.05	nd	0.04	27	27
Toholampi (sandy silt loam)[b]	1440-2160	144	<0.02		0.07	7-9	7-9
Toholampi (sandy silt loam)[c]	1000	8	0.087	35.4	0.26	39	73

[a]Time from glyphosate application.
[b]Background residue.
[c]Residues from current study.

At Toholampi, glyphosate had been applied in autumn 1989, 12 years before the current study (Chapter 5). However, the background concentration of AMPA was only 40% lower than in Janakkala and even 43% higher than that in Perniö, where the latest applications were done 8 and 18 months, respectively, before the first sampling (Table 7.6). In the 1980s, the glyphosate application rate was higher (typically 1.5-2.5 kg ha^{-1}) than used in the current study. Thus, the background residue of AMPA corresponds to 7-9% of those application rates, indicating a surprisingly slow degradation rate and high aging potential for AMPA. Another plausible explanation for the background residues is deposition of glyphosate transported with spray drift. But even though the Toholampi experimental field is situated in a region where the use of glyphosate is common and spray drift is likely, high residues like this were unexpected. However, compared to Fomsgaard et al. (2003) and Simonsen et al. (2008), the residues were somewhat similar. Fomsgaard detected background concentrations of AMPA, but not of glyphosate, in soil from fields sprayed 3 and 5 years earlier, and Simonsen et al. (2008) found aged residues 0.81 ng g^{-1} glyphosate (corresponding to 0.34% of applied amount) and 10.46 ng g^{-1} AMPA (corresponding to 4.36% of applied glyphosate, using molar conversion) in soil 21 months after application. In their study, the detection limits were 0.04 ng g^{-1} for glyphosate and 0.02 ng g^{-1} for AMPA.

7.2.4 Glyphosate movement in the soil profile

In all trials, glyphosate and AMPA residues were found below the plough layer. In Toholampi, 38 days after application, glyphosate residues were found in the soil layer 0-35 cm, and residues of AMPA were found at a depth of 0-60 cm (Chapter 5, Table 4). Glyphosate and AMPA residues were not later quantified below 35 cm. However, 388 and 613 days after glyphosate application, traces of both glyphosate and AMPA residues were detected at the depth of 35–60 cm (Chapter 5, Table 4). In Janakkala and Perniö, both glyphosate and AMPA residues were found at the depth of 0-50 cm. In addition, in Janakkala, glyphosate was detected also at the depth of 50-70 cm (Chapter 4, Table 7). Similar results have been reported by Fomsgaard et al. (2003). In their lysimeter study, residual concentrations of glyphosate and AMPA were found two years after application at depths between 70 and 90 cm.

In our study, a rapid transport of glyphosate from the soil surface was observed soon after application (Chapters 4 and 5) at all study sites. These findings were unexpected, because the soils were very dry and no rainfall had occurred between applications and soil samplings, which made glyphosate movement with water in the soil profile unlikely. Because glyphosate is translocated from foliage to roots and then released to soil, we postulated that this could be a potential explanation for the residues. This phenomenon is further discussed in Section 7.3.

7.2.5 Glyphosate dissipation in the field

Background residues of glyphosate and AMPA complicate the assessment of degradation rate, because the residues of the recent and previous applications cannot be separated. Although autumn application resulted in a similar slow dissipation at all study sites, the degradation rate was different during summer. Quite rapid dissipation during growing seasons was shown in Janakkala and Perniö (Chapter 4, Table 7, Figure 6), whereas in Toholampi (sandy silt loam) the dissipation of glyphosate was relatively slow also during the summers, and the accumulation of AMPA was detectable already after the first autumn (Figure 7.3, see also Chapter 5, Table 4).
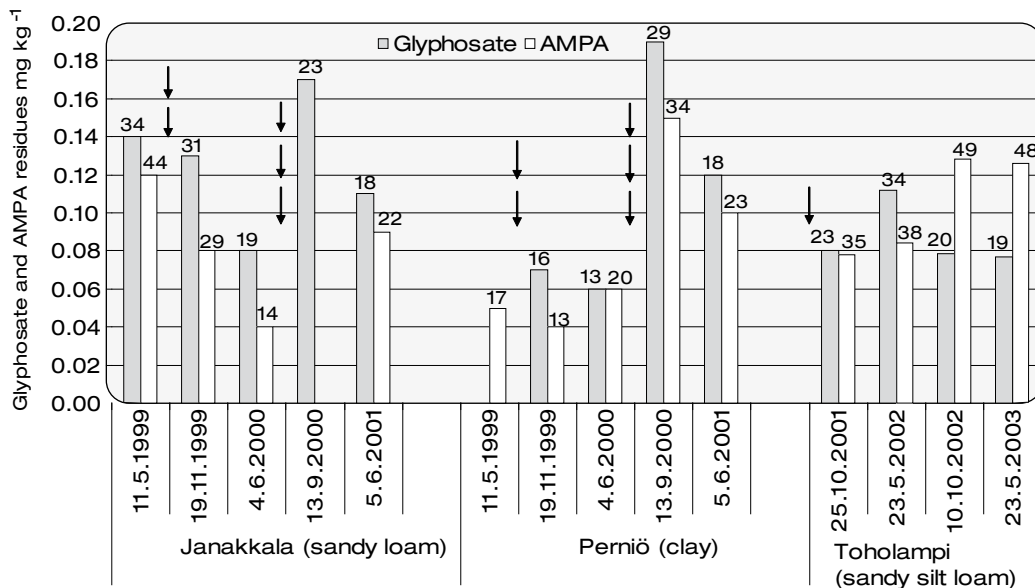
Figure 7.3. Glyphosate and AMPA residues (mg kg-1 dw) in the plough layer (0-30 cm in Janakkala and Perniö and 0-25 cm in Toholampi) and their proportion (%) of the annual applied amount of glyphosate. The proportion values are given on top of the columns. In Janakkala and Perniö, glyphosate was applied in June and July (Table 7.5). In Toholampi, only one application was done (17.09.2001). The arrows show the application times.

The results of the field studies with sugar beet show clear over-winter persistence of glyphosate and AMPA even when the glyphosate applications had been made already in June-July, allowing a longer period of time for degradation. Taking account of the total use of glyphosate (including background residues), about 10 to 20% of glyphosate was detected at the end of the study in both soils, demonstrating that the time for 90% field dissipation (DT90) of glyphosate was approximately 11 months (Chapter 4, Figure 6) in Janakkala and Perniö. Considering only the applications made in the previous summer, the residues of glyphosate represented about 18% and those of AMPA 22% of the applied glyphosate (Figure 7.3). In Toholampi, the residues of glyphosate and AMPA together corresponded to 67% of the applied amount of glyphosate still 20 months af-

ter application (Figure 7.3, see also Chapter 5, Table 4).

7.2.6 Glyphosate and AMPA ratios

The degradation rates and accumulation of a herbicide in soil can be illustrated by the molecular ratio of the residues of the compound and its metabolite with time. A decreased glyphosate/AMPA ratio indicates a faster degradation of glyphosate and a higher stability of AMPA (Grunewald et al. 2001). Thus, relative accumulation of AMPA is evident when the ratio is considerably below one. This kind of examination also enables comparison of herbicide degradation in contrasting soils. Naturally, soon after application the proportion of glyphosate is higher, but it ought to diminish with time. The results for glyphosate/AMPA ratios in the current studies are given in Table 7.7.

Table 7.7. Glyphosate/AMPA ratios in the plough layer. The time from the last application is given in parentheses.

Site	Depth (cm)	Glyphosate/AMPA				
		11.5.1999	19.11.1999	4.6.2000	13.9.2000	5.6.2001
Janakkala (sandy loam)[a]	0-28	(8 months)	(4.5 months)	(11 months)	(2 months)	(11 months)
		0.77[b]	1.07	1.31	[c]	0.81
Perniö (clay)[a]	0-28	(27 months)	(4.5 months)	(11 months)	(2 months)	(11 months)
		[b d]	1.14	0.66	0.60	0.79
Toholampi (sandy silt loam)[e]	0-25	25.10.2001	16.5.2002	23.9.2002	10.10.2002	23.5.2003
		(1 month)	(8 months)	(12 months)	(13 months)	(20 months)
		0.65	0.87	0.68	0.40	0.40

[a]Glyphosate applications were done in June-July 1999 and 2000.
[b]Based on background concentrations.
[c]Only glyphosate was detected in the soil profile.
[d]Only AMPA was detected.
[e]Application of glyphosate was done on 17 September 2001.

Interestingly, during the first summer at the Janakkala (sandy loam) and Perniö (clay) sites the degradation rates for both compounds were nearly in balance. Thereafter it was lower for AMPA in Perniö until the end of the study, indicating that in the clay soil the accumulation risk of AMPA is higher than that of glyphosate. In sandy loam in Janakkala, the accumulation risk was evident only at the end of the study.

In Toholampi the degradation rate of AMPA was lower than that of glyphosate over the whole study period; at the end of the study the residues of glyphosate and AMPA corresponded to 23% and 53% of the applied amount, respectively (Chapter 5, Table 4). It has to be remembered that after the first winter the degradation of these compounds was slower in Toholampi than at the other study sites. Anyway, all results provided evidence that AMPA was more persistent and had a higher accumulation tendency than glyphosate. This agrees with the results of Fomsgaard et al. (2003) who recovered about 1% of glyphosate but as much as about 35% of AMPA two years after glyphosate treatment in their outdoor lysimeter study. Also Grunewald et al. (2001) reported AMPA to be more persistent than glyphosate.

7.2.7 Glyphosate losses in runoff waters

In the leaching study in Toholampi, the concentrations of glyphosate, AMPA and phosphorus in the surface and subsurface leachate waters were monitored (Chapter 5) in the field in order to examine the magnitude of their losses at field level. Our hypothesis was that owing to their similar reaction mechanisms (e.g. Piccolo and Celano 1994; Gerritse et al. 1996; Gimsing and Borggaard 2001; Wang et al. 2005), these compounds could show similar leaching patterns. If so, it should be possible to approximate losses of glyphosate on the basis of phosphorus losses.

In the first winter, the glyphosate loss into surface runoff water was about 0.4% of the applied amount, with the highest concentrations and the major part of the herbicide loadings (99%) obtained during the

snow melting and soil thawing period. The detection limit for glyphosate and AMPA analysis was 0.1 µg L^{-1} in runoff water. The average concentration in the first winter was as high as 2.9 µg L^{-1} for glyphosate and 0.3 µg L^{-1} for AMPA (Chapter 5, Table 5), clearly exceeding the EU threshold value for drinking water (0.1 µg L^{-1}). The threshold value was still exceeded in the second winter. Siimes et al. (2006) obtained comparable results in the Toholampi field: about 0.1% of glyphosate applied in July was found in surface water within ten months. Glyphosate concentration in surface runoff water was highest in the first runoff event, 18 days after application, and the majority of the loading was obtained in the snow melting period. Contrary to our study, in the winter the glyphosate concentration did not exceed 1 µg L^{-1} (Siimes et al 2006). During the experiment (from 17 September 2001 to 23 April 2003), the total loss of glyphosate was 5.12 g ha^{-1} and that of AMPA 0.48 g ha^{-1}, corresponding to 0.51 and 0.073% of the applied amount of glyphosate, respectively.

In our study, soil management practices greatly affected the glyphosate losses. The soil was not ploughed after the application of glyphosate before the first winter, leaving much of the applied glyphosate in a very shallow surface soil layer. This practice probably increased the losses with surface runoff during the first winter. When soil was ploughed the next spring, the glyphosate-rich soil surface and plant residues were turned down, and after that the losses with surface runoff were lower. Previous studies in the Toholampi experimental field showed that ploughing increased subsurface transport (Turtola et al. 2007) and the leaching risk of pesticides with subsurface drainflow (Laitinen 2000) and, thus, the risk of groundwater pollution. In the

current study, due to the drought during the study period there were only two small subsurface drainflow events and no residues of glyphosate or AMPA were detected in these water samples.

The chemical concentrations exceeding the threshold values are a matter of concern, because in Finland (and many other countries) a large part of the household water derives from surface water bodies. Although the concentrations are diluted when mixed in with surface water bodies, they may lead to temporary pollution of surface waters. This was shown in the Finnish water monitoring programme that started in 2008: residues of glyphosate and AMPA were detected in October, the concentration being 0.22 µg L^{-1} for glyphosate and 0.46 µg L^{-1} for AMPA (Siimes K., unpublished). Similarly e.g. in Norway, Sweden, Denmark and the Netherlands (Ludvigsen and Lode 2001; Törnquist et al. 2002; Adriaanse et al. 2008) glyphosate and AMPA residues are also frequently found in monitoring programmes.

In our study, a significant positive correlation between glyphosate and phosphorus concentrations in surface runoff water was found (Chapter 5, Table 6). The key factors promoting the binding and reducing the leaching of glyphosate appeared to be climatic conditions, low soil P status and high Al and Fe oxide contents, and low DPS. Cold winters and dry summers slowed the degradation rate. It is possible that losses are much higher from phosphorus-rich fields as was concluded in Chapter 3. Also Simonsen et al. (2008) assumed that the leaching risk for glyphosate is greater in fertilized soil. However, more laboratory and, preferably, field studies are needed to clarify the relationships of these factors.

7.3 Glyphosate translocation from plants to soil

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. In this study, its translocation in plants was monitored in a leaching field trial and in a glasshouse trial (Chapters 5 and 6). In addition, the fate of glyphosate was simulated with the PEARL 3.0 model and compared with a glasshouse trial. The glasshouse pot study was conducted with an annual plant, quinoa, *(Chenopodium quinoa,* Willd) that is closely related to lamb's quarters (*Chenopodium album,* L.*)*, a common annual weed in Finnish fields. In the leaching field study, glyphosate residues were analysed in roots of quackgrass [*Elymus repens* (L.) Gould], the most common perennial weed in Finland.

The results of this thesis show that translocation from plants foliage to roots plays a significant role in the fate of glyphosate in soil. Results from sugar beet field studies indicated glyphosate translocation within the plant (Chapter 4) and results from glasshouse pot and leaching field experiments confirmed this (Chapters 5 and 6). In the glasshouse pot study (Chapter 6), where soil contamination with glyphosate was prevented, 0.3 and 1.1% of the applied amount of glyphosate was found in the soil surface layer (depth 0-1.0 cm) one hour after the application.

At that time the deeper layers were not sampled. Eight days later when the plants were dead, the glyphosate residues in the root samples collected from the whole pots (depth 0-14 cm) corresponded to up to 12% of the applied amount and, at the same time, the residues in the soil accounted for 4%. Therefore, the combined glyphosate residue transported by the plant to the soil was 16% of the applied amount. A similar proportion of transported residues (about 15%) was observed (estimated as difference of applied amount of glyphosate and amount of residues in soil) in the leaching field study 38 days after the application (Chapter 5).

According to these results, the penetration and translocation of glyphosate were quite rapid (Chapter 6), which agrees with previous studies. According to Sprankle et al. (1975b), foliage absorption of glyphosate in 3-4-leaf quackgrass plants occurred most rapidly within 4 hours and continued to increase but not significantly until monitoring was ended at 48 hours. The translocation rate to rhizomes and shoots was about 2% per hour within 24 hours after treatment and continued to decrease until the end of the study, the total being 66.7% of foliage absorbed glyphosate and, thus, 35% of the applied amount of glyphosate. Geiger et al. (1999) found a rapid initial uptake and translocation of glyphosate by sugar beet plants. The initial rate of export from source leaves into sinks reached a maximum after 2 to 3 hours. About 5.5% of the total absorbed glyphosate was translocated per hour in glyphosate-susceptible plants, giving 7% of the applied amount translocated in the 24-h observation period. Arnaud et al. (1998) reported that about 22% of the applied amount of glyphosate was exported to roots. According to Schultz and Burnside (1980) and Alister et al. (2005), 52% and 22%, respectively, of the foliage-absorbed glyphosate was found in the roots. Differences in plant species, growth stages and duration of observation may partly explain the variation of these results. In general, when observation lasted several days, the foliar absorption seemed to be about 50% of the applied amount.

The results of our two trials were surprisingly similar. However, despite the similarities the results cannot be directly generalized. In cultivated fields the quantitative ratio of canopy and roots varies and thus

the amount of glyphosate translocated to roots compared to the field area and soil volume varies as well from case to case. For instance, when grass and green set-aside land is treated with glyphosate for close down, the canopy coverage is very high and most of the herbicide remains on the leaves and is further translocated to the roots, whereas in glyphosate sprayings at the beginning of the growing season a much larger amount of the herbicide ends up directly on the soil surface. In addition, environmental factors, such as temperature and relative humidity, may affect both glyphosate foliar absorption and translocation (Feng et al. 1999; Reddy 2000; Sharma and Singh 2001).

In our studies, in spite of differences in the growth form of the plant species, the different growth stages and growth circumstances, approximately the same proportion of the applied glyphosate was translocated to the roots (Chapters 5 and 6). In the pot study the glyphosate concentration in the quinoa roots was 9.40 mg kg^{-1}, over 500 times the concentration in the soil, whereas in the leaching field study the mean concentration of glyphosate in the quackgrass roots was 2.68 mg kg^{-1}, about 50 times higher than the concentration in the soil at a depth of 5-25 cm. The greater mass of the quackgrass roots may explain this result.

The published information about glyphosate degradation in plants is somewhat contradictory. In general, it has been stated that glyphosate does not degrade in living plant cells or the degradation is insignificant (e.g. Eberbach and Bowner 1995). The results of our studies are consistent with this conclusion; no AMPA residues were found in the root samples (Chapters 5 and 6), but degradation took place when in contact with soil microbes. However, Putnam (1976) concluded that a small amount of glyphosate had been metabolized by apple and pear trees. Sprankle et al. (1975b) and Sandberg et al. (1980) observed degrada-

tion in some weed plants, but they pointed out that the data do not unequivocally indicate metabolism of glyphosate by the plant. Reddy et al. (2004) found very low amounts of AMPA in genetically modified, glyphosate-resistant soybean leaves, and they suggested that plant injury was caused by AMPA formed from glyphosate degradation in the plant. Anyway, too little is known about the degradation of glyphosate in glyphosate-susceptible plants (weeds and crops) considering the huge amounts of glyphosate used.

The translocation can also take place in circumstances where no leaching occurs in the soil and glyphosate can end up in deeper soil layers or root zones quite rapidly compared to leaching. Thus, some unexpected results could be explained by translocation. These include, for instance, the occurrence of glyphosate residues in the deeper layers of soil during a dry period following glyphosate application (Chapters 4 and 5). The environmental fate and impacts of residues depend on the depth of the root zone, the hydraulic conditions of the field site and the capacity of soil micro-organisms to degrade glyphosate and its metabolites.

The efficacy of glyphosate as a systemic broad-spectrum herbicide is based on translocation to sensitive parts of the plants and inhibition of modes of action of key enzymes in the plant. Only effective translocation of glyphosate in plants gives good control of glyphosate-sensitive weeds. From this point of view, the occurrence of glyphosate in roots is most desirable, but at the same time it is a sign of soil contamination and leaching risk. The translocation process should be included in risk assessment and models. The results of the present studies suggest that residues of glyphosate in root samples might be one way of predicting those risks. However, more studies are needed to develop this method.

7.4. Factors affecting the fate of glyphosate in agricultural fields

7.4.1 Soil properties

Soil properties, such as organic carbon content, pH, Al and Fe oxides, phosphorus and phosphorus fractions are considered to be factors determining glyphosate sorption and thus its bioavailability and degradation. In the current study, these factors did not explain the differences in glyphosate degradation between the study sites. In fact, by normalizing for organic carbon content, the values indicated a similar or lower adsorption potential for the sandy silt loam (Toholampi) than for the other soils (quite similar pH and DPS, lower oxide content, higher phosphorus status and inorganic P fractions) (Table 7.8). However, the adsorption coefficient was highest in the sandy silt loam (Toholampi) (K_F 159), demonstrating stronger adsorption and lower mobility in laboratory test conditions.

The normalization of sorption for soil organic carbon (K_{FOC}) demonstrated slightly greater adsorption in the plough layer of Toholampi than in the other fields (Table 7.8). However, we assumed that organic carbon (OC) content had only a small effect on adsorption and that it could not explain the variation of the fate of glyphosate in the soils (Chapter 2). For example, even though the OC content was lower in the subsoil than in the plough layer, the

Table 7.8. Selected soil properties in plough layers of the experimental fields.

Property	Janakkala Sandy loam	Perniö Clay	Toholampi Sandy silt loam
Organic carbon content (%)	5.9	7.1	5.0[a]
pH_{water}	6.4	6.02	6.2
AL oxides (mmol kg^{-1})	186	84	96
Fe oxides (mmol kg^{-1})	76	132	30
P_{TOT} (mg kg^{-1})	1130	1310	373
P_{AC} (mg L^{-1})	3.3	4.1	7.5
P_{NH4F} (mg kg^{-1a})	191	48	91
P_{NaOH} (mg kg^{-1a})	113	160	176
DPS (%[b])	7.5	6.2	7.1
K_F (L kg^{-1})[c]	97	97	159
K_{FOC} (L kg^{-1})[d]	1643	1374	2014[e]

[a]Soil organic carbon content in the leaching study.

[a] Inorganic P fractions: P_{NH4F} is assumed to be bound by Al oxides and P_{NaOH} by Fe oxides.

[b]Degree of P saturation. Calculated as a molar ratio of $(P_{NH4F} + P_{NaOH}) / [0.5*(Al_{OX} + Fe_{OX})]$.

[c]Freundlich adsorption coefficient for glyphosate.

[d]Glyphosate adsorption coefficient based on organic carbon content.

[e]Soil organic carbon content for calculete K_{FOC} was 7.9%.

adsorption was equal (Perniö) or higher (Janakkala and Toholampi) in the subsoil (Table 7.2). In addition, according to our adsorption tests of 21 soils, the adsorption was very high (K_{FOC} >5000) in the subsoils that contained less than 1% of OC (Table 7.2). Our assumption is in line with the literature. Borggaard and Gimsing (2008) concluded that soil organic matter seems not to sorb glyphosate but that it may indirectly affect the sorption. They also concluded that glyphosate is bound strongly to Al and Fe oxides but that its competition with phosphate for sorption sites varies from soil to soil and that it is difficult to draw general conclusions about glyphosate behaviour in soils.

The degradation rate of glyphosate usually correlates with the general microbial activity, but in the current study microbial activity was not measured. It is likely, however, that it was higher at the sugar beet cultivation sites (Janakkala and Perniö) where a greater amount of plant residues was mixed annually into the soil than at the sandy silt loam site (Heinonen-Tanski et al. 1985 and 1989).

For the sugar beet cultivation (Janakkala and Perniö), the glyphosate applications were carried out in June and July when dissipation (mainly via biodegradation) is rapid compared to post-harvest dissipation (see Figure 7.3). The earlier the application, the relative smaller amount persisted over winter. In the leaching field study (Toholampi) the application was done in autumn when, as discussed above, the formation of bound or aged residues is more likely. Unfavourable climatic conditions for the soil microflora during this study also reduced the possibility of degradation of glyphosate and AMPA. The clear difference in seasonal dissipation (summer *versus* au-

tumn and winter) shows that early applications have certain benefits concerning degradation under Finnish conditions.

7.4.2 Cultivation practices

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 or autumn application, or their combination when reduced tillage cultivation or no till is used instead of ploughing. Spring and early summer sprayings allow better conditions for glyphosate degradation, but repeated applications on the soil surface without deep tillage may lead to accumulation, especially in the surface soil. In the 1970s, besides autumn application, glyphosate was commonly used in midsummer when the growth-stage of plants is favourable for glyphosate translocation in the plant, which gives good weed control. Currently this practice is rare, but it should be recommended to fit into crop rotation.

In reduced tillage and no till cultivation, fertilizer phosphorus accumulates in the soil surface (Pitkänen 1988; Alakukku et al. 2004). This may decrease glyphosate adsorption and thus increase degradation (bioavailability) and mobility in the soil surface and, perhaps, in the soil profile and lead to losses with surface water. On the other hand, it is supposed that water circulation in the soil profile is improved by reduced tillage, and this may lead to glyphosate losses to groundwater, especially in structured soils (Al-Rajab et al. 2008). The effects of soil management practices, soil phosphorus status and phosphorus saturation (DPS) on glyphosate behaviour are illustrated in Figure 7.4.

High

	Plough	No till
	1 • Lower adsorption and high desorption. • Higher degradation rate. • Higher mobility. • Higher losses, mainly in subsurface water.	**2** • Lower adsorption and higher desorption. • Higher degradition rate. • Higher mobility. • Higher losses, mainly in surface water.
	3 • High adsorption and low desorption in plough layer. • Low degradation rate. • Low mobility. • Low losses, mainly in subsurface water. • Repeated application may lead to accumulation in plough layer. • Janakkala, Perniö and Toholampi	**4** • High adsorption and low desorptionin in soil surface. • Low degradation rate. • Low mobility. • Low losses, mainly in surface water. • Repeated application may lead to accumulation in soil surface. • Toholampi

P status and DPS
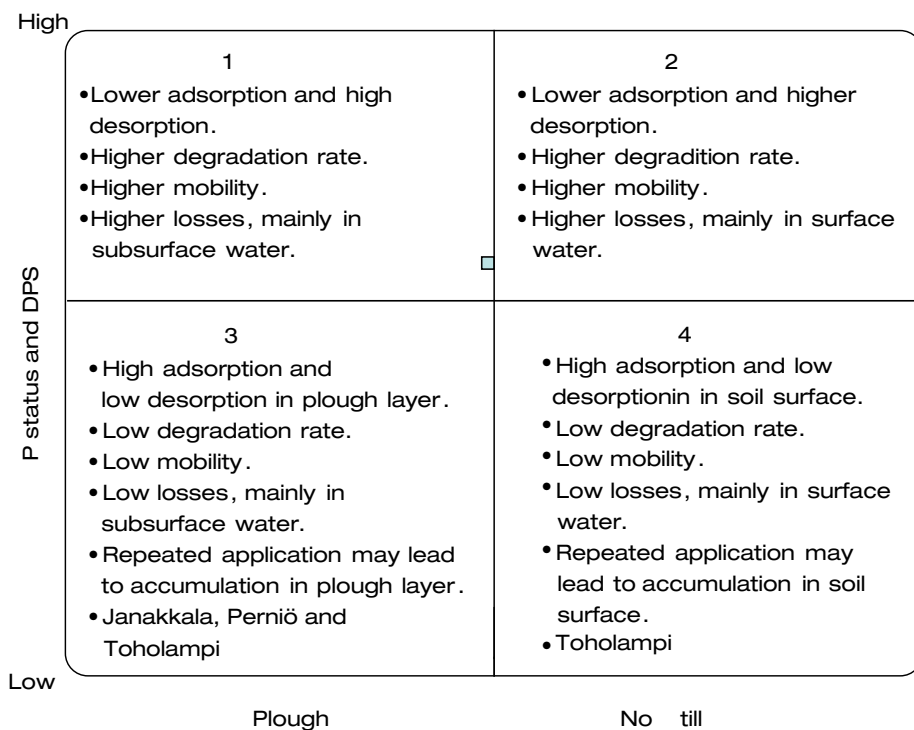
Low

Plough   No   till

Figure 7.4. Schematic presentation of the relationships between soil management practices and soil P status and the degree of P saturation (DPS) to the fate of glyphosate in the plough layer. The studied sites are located in box 3, except Toholampi (sandy silt loam) which was in box 4 at the beginning of the study before ploughing.

7.5 Comparison of herbicides in conventional and genetically modified sugar beet cultivation

In theory, replacing conventional crops with genetically modified (GMO), glyphosate or glufosinate-ammonium-resistant crops allows reduction of the number of herbicides and also the total amount of herbicide used. In our sugar beet study (Janakkala and Perniö), glyphosate and glufosinate-ammonium replaced three conventional crop herbicides (phenmedipham, ethofumesate and metamitron). The annual uses were 1440-2160, 800-1200 and about 3000 g ha^{-1} for glyphosate, glufosinate-ammonium, and the total use of the three other herbicides, respectively (Chapter 4). Thus, cultivation of GMO plant species resistant to glyphosate may diminish the total water contamination risk and, thus, be an option in water protection strategy. On the other hand, expanded long-term use of glyphosate could elevate its concentrations in water sources.

In our study, over 90% of the applied glufosinate-ammonium was dissipated within 2.5 months and more than 80 and 95% of the applied phenmediphan and metamitron, respectively, were dissipated by harvest. In contrast, ethofumesate and glyphosate seemed to accumulate in the soil. During the study with no background contamination, between 30 and 55% of annual applied ethofumesate and 10-20% of glyphosate (and 8-10% of AMPA) were found at both study sites in the subsequent spring. The overall observed order of persistence in soil was: ethofumesate > glyphosate > phenmedipham > metamitron > glufosinate-ammonium.

Herbicide mobility and leaching risk are commonly assessed using the Freundlich adsorption coefficients (K_F). The K_F values determined for the studied soils suggested that the mobility of glyphosate and phenmedipham was low in the Janakkala and Perniö fields, while the expected mobility of glufosinate-ammonium, ethofumesate and metamitron varied from moderate to high. The herbicides could be arranged according to their adsorption coefficients as follows: glyphosate > phenmedipham > ethofumesate ≈ glufosinate-ammonium > metamitron, with metamitron having the highest risk of leaching (Chapter 2). However, in the field study, glyphosate and phenmedipham were the most and glufosinate-ammonium the least mobile in the soil profile (Chapter 4). Translocation of glyphosate from plants to soil explains part of the glyphosate transport through the soil matrix (Chapters 4 and 6), and rapid degradation is assumed to account for dissipation of glufosinate-ammonium (Smith and Belyk 1989; Behrendt et al. 1990). In the current sugar beet cultivation study, no indication was seen during the two-year experiment of a potential groundwater pollution risk, but herbicides may cause surface water pollution.

7.6 Uptake of glyphosate residues by plants – does it cause adverse effects on the crop yield or consumers?

Because both glyphosate and AMPA are generally considered to be non-toxic for soil organisms, threshold concentration values for glyphosate in soil are not set. However, in the leaching field study, both glyphosate and AMPA residues were alarmingly high at the beginning of the subsequent growing seasons. This raises the question of whether those residues will have negative effects on the subsequent crop.

Simonsen et al. (2008) reported that also aged glyphosate residues can be taken up by plants. In their study, glyphosate and AMPA residues were still available for plant uptake six months after application. The concentrations of glyphosate and AMPA residues taken up by rape and barley crops were less than the Acceptable Daily Intake (ADI) for consumers. ADI has been set to 0-0.3 mg kg^{-1} /body weight by the WHO/FAO (1996). The growth period was short (41 days) compared with the period common in agriculture and the authors pointed out that during a longer period more residues would probably be taken up. However, they postulated that the aged residues originating from normal spraying practice for glyphosate do not seem to pose a risk for the crop yield or consumers. In the current study, plant uptake was not studied. In our study, the high concentration of glyphosate and AMPA residues in the soil suggests that for risk assessment there is a need to examine the residue uptake by crop plants.

7.7 Assessment of the environmental fate of glyphosate

The fate of pesticides in the environment has recently been discussed in the context of global climate change. The most likely scenario in Finland is that our summers will be increasingly warm and dry and winters increasingly mild and rainy. This will mean more dry summers such as that of 2002 in Toholampi (Chapter 5) when the degradation rate of the glyphosate residues was very low and the formation of aged residues was high. In a rainy and mild winter, if the soil is not frozen, both surface and subsurface water flow will increase which might increase the risks of contamination of water sources. Transport of strongly sorbed compounds from the field to the aquatic environment can occur as solutes or bonded to soil colloids. Both forms can be moved in the soil by surface and subsurface transport, thus forming a risk of water pollution (Borggaard and Gimsing 2008).

Translocation through plant and residues in dead root mass has a significant role in controlling the fate of glyphosate in soil; more than 12% of the applied glyphosate was found in the roots (Chapter 6). Although translocation of glyphosate and exudation from intact roots to soil are well known, there are no studies on the role of these processes in the transport and occurrence of residues in soil. Our study was the first one concerning this possibility. Translocation can take place also in dry circumstances where no leaching occurs in the soil and glyphosate may quite rapidly end up in deeper soil layers or root zones. This could explain some of the mysterious results in our field experiments and was clearly shown in our pot study. Translocation should be included both in leaching risk assessments and fate models of glyphosate (and other systemic pesticides).

The adsorption tests revealed that the adsorption of glyphosate decreases and the mobile fraction drastically increases when soil phosphorus status increases from low to excessive (Chapter 3). On the other hand, the strong adsorption indicated a low degradation rate and high accumulation risk. The key soil factors promoting the persistence and reducing the leaching of glyphosate and AMPA appeared to be low P status and high Al and Fe oxide contents, leading to a low degree of P saturation (DPS). These results were confirmed by field studies where a significant positive correlation was observed between glyphosate and phosphorus concentrations in surface runoff water (Chapter 5). The close correlation between P_{AC} and K_F values indicated that the soil phosphorus status can be utilized in environmental risk assessment for glyphosate (Chapter 3). Because the phosphorus status of fields is determined in Finland at regular intervals within the agri-environmental programme, a large amount of data on the P_{AC} values is available for risk assessment at farm level and often at plot level, too.

A statistical model of the relationship between soil P_{AC} values and glyphosate adsorption coefficient (K_F) was developed and fitted using the adsorption data set obtained (Chapter 3). The model was tested with the independent Finnish data set. The developed model fitted the data set rather well when the soil P status was good or high, but it underestimated the sorption when the P status was very low and the K_F value simultaneously very high. The equations may be a useful tool in assessing the leaching risks of glyphosate when P_{AC} is at good and high levels, but it is obvious that the equations are not useful for all soil types, and they must be calibrated before being used for assessing the leaching risks of glyphosate.

The prolonged or repeated use of herbicides having a high sorption tendency may lead to their accumulation. In the current study, the extent of uptake of glyphosate residues

by plants was not studied, but alarmingly high concentrations of aged glyphosate and AMPA residues recovered in the soils raise the question of whether those residues will have a negative effect on the subsequent crop and, in the worst case, on consumers. Recent investigations indicate negative side-effects on non-target plants (Guldner et al. 2005; Neuman et al. 2006). For risk assessment there is a need to examine also this possibility.

In addition to climatic conditions (e.g. dry *vs.* rainy summers, cold *vs.* mild winters) also the time of application proved to have a major effect on the behaviour of glyphosate, with a clear difference between early-season and autumn application. Under normal weather conditions, early application proved to diminish the environmental risk under Finnish conditions. However, even when the applications were done in June-July, allowing a longer period of time for degradation, glyphosate and AMPA still showed a clear overwinter persistence. Autumn application poses a greater environmental pollution risk through accumulation and leaching. Therefore, application in late autumn should be critically evaluated and, depending on soil management practices, limitations or restrictions should be set for the most critical fields. Glyphosate gives good results in weed control, but from the environmental point of view it is important to identify fields where the glyphosate risks are obvious, and special regulations or restrictions should be applied. Above all, suitable application practices for different soils and crop rotations should be sought.

7.8 Conclusions

The following conclusions can be drawn from the present field studies:

1. The sorption of glyphosate varies widely between different soils and it may vary also layer by layer, which should be taken into consideration when predicting the risk of leaching through the soil matrix.

2. According to the sorption tests, glyphosate is classified as a highly adsorbed and immobile compound in soils of low phosphorus status, but the amount of mobile and leachable glyphosate increases with increasing phosphorus status.

3. Strong adsorption to and low desorption from soil suggest that the risk of glyphosate leaching through the soil matrix is minimal when the soil P status is low. On the other hand, strong adsorption reduces the bioavailability (degradation) of glyphosate and can lead to accumulation in soil if glyphosate application is repeated.

4. The correlations between the Freundlich adsorption coefficients (K_F) obtained in the adsorption tests and P_{AC} were nonlinear but high. The equations may be a useful tool in assessing the leaching risks of glyphosate when P_{AC} was at good and high levels. The equations must be calibrated before being used for assessing the leaching risks of glyphosate.

5. A significant **positive** correlation was observed between glyphosate and phosphorus concentrations in surface runoff water. The key factors controlling the degradation and leaching of glyphosate appeared to be low soil P status and high Al and Fe oxide contents, a low degree of P saturation (DPS) and climatic conditions, e.g. cold winters and dry summers.

6. To assess the accumulation and leaching risks, easy and economical methods based on the behaviour of glyphosate should be further studied. The Agri-Environmental Programme in Finland checks the P status of fields at regular intervals. Thus, there is a large amount of data available on P values obtained by acid ammonium acetate extraction (P_{AC}), the method used in this routine soil testing.

7. The dissipation rates for glyphosate in Finnish soils during the growing season do not differ from those observed in Central Europe and Northern America when glyphosate is applied at the beginning of the growing season (from May to July), but repeated applications can lead to accumulation in the soil also after early-season applications.

8. Autumn application causes an environmental pollution risk by accumulation in the soil and, depending on soil management practices, by losses of glyphosate into surface or subsurface waters. Therefore, application in late autumn should be critically evaluated and limitations and restrictions should possibly be set for the most critical fields.

9. Glyphosate translocation through plant to root and residues in dead root mass has a significant role in the transport and occurrence of glyphosate residues in soil and should therefore be included in models and risk assessments.

10. The behaviour of aged residues of glyphosate and AMPA in soil, their uptake by plants and effects on subsequent yields need to be examined.

11. Glyphosate gives good results for weed control. Therefore, concerning both environmental health and efficacy of weed control it is important to identify fields where risks are obvious and special regulations or restrictions should be applied. Above all, suitable application practices for different soils and crop rotations should be sought.

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