

Spatial variation in herbicide leaching from a marine clay soil via subsurface drains

Barbro M Ulén,* Mats Larsbo, Jenny K Kreuger and Annika Svanbäck

Abstract

BACKGROUND: Subsurface transport via tile drains can significantly contribute to pesticide contamination of surface waters. The spatial variation in subsurface leaching of normally applied herbicides was examined together with phosphorus losses in 24 experimental plots with water sampled flow-proportionally. The study site was a flat, tile-drained area with 60% marine clay in the topsoil in southeast Sweden. The objectives were to quantify the leaching of frequently used herbicides from a tile drained cracking clay soil and to evaluate the variation in leaching within the experimental area and relate this to topsoil management practices (tillage method and structure liming).

RESULTS: In summer 2009, 0.14, 0.22 and 1.62%, respectively, of simultaneously applied amounts of MCPA, fluroxypyr and clopyralid were leached by heavy rain five days after spraying. In summer 2011, on average 0.70% of applied bentazone was leached by short bursts of intensive rain 12 days after application. Peak flow concentrations for 50% of the treated area for MCPA and 33% for bentazone exceeded the Swedish no-effect guideline values for aquatic ecosystems. Approximately 0.08% of the glyphosate applied was leached in dissolved form in the winters of 2008/2009 and 2010/2011. Based on measurements of glyphosate in particulate form, total glyphosate losses were twice as high (0.16%) in the second winter. The spatial inter-plot variation was large (72–115%) for all five herbicides studied, despite small variations (25%) in water discharge.

CONCLUSIONS: The study shows the importance of local scale soil transport properties for herbicide leaching in cracking clay soils.

© 2013 The Authors. *Pest Management Science* published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.

Keywords: bentazone; clopyralid; glyphosate; fluroxypyr; MCPA; subsoil

1 INTRODUCTION

Subsurface transport from agricultural land via tile drains can significantly contribute to pesticide contamination of surface waters. Such leaching losses commonly represent < 1% of applied amounts,^{1,2} but may be considerably larger from clay soils³ and erosion-prone silty soils.⁴ The amount of leaching is to a large extent determined by pesticide properties where weakly sorbed, slowly degrading compounds pose the greatest risk of leaching. The groundwater ubiquity score (GUS) is a simple leaching risk indicator for pesticides.⁵ It combines the pesticide adsorption distribution coefficient to organic carbon (K_{oc}) and the degradation half-life (DT_{50}). In addition to pesticide properties, the losses are largely dependent on soil properties and hydrological characteristics, with preferential flow in cracking soil types perhaps being the worst-case scenario.² As a result, pesticide losses vary considerably at the catchment scale.^{6,7} Variation in hydrological field properties (e.g. water retention capacity and tendency for topsoil saturation) is also very important and can explain the large variation in pesticide losses observed at the catchment scale.⁶ However, solute transport may also vary as a result of subsoil characteristics, as indicated by field dye-tracer experiments.⁸

The main aim of this study was to quantify leaching of some frequently used herbicides from a tile drained cracking soil as a result of naturally occurring rainfall and snow accumulation. A second aim was to evaluate the variation in leaching within

the experimental area and relate this to topsoil management practices.

2 MATERIALS AND METHODS

The field site is located in a flat valley (mean slope less than 0.05%) with a clay soil of marine origin in eastern Sweden. The experimental field (1.3 ha) with 28 plots (24 m × 20 m) was tile-drained in 2006 to 0.9 m depth (8 m spacing).⁹ Twenty-four of these plots were used in the present experiment. The plots are situated in two rows of 14 plots at varying distance from an open ditch that acts as the recipient of drainage water from the surrounding valley (Figure 1). Three management practices were randomly assigned to the plots: Conventional autumn ploughing, shallow autumn tillage and structure-liming (i.e. liming carried out to reduce phosphorus leaching and to improve crop yield by improving soil structure). The soil is strongly aggregated, especially in the lower subsoil (43–100 cm depth) where aggregates are

* Correspondence to: Barbro M Ulén, Department of Soil and Environment, Swedish University of Agricultural Sciences, PO Box 7014, SE-750 07 Uppsala, Sweden. E-mail: barbro.ulen@slu.se

Department of Soil and Environment, Swedish University of Agricultural Sciences, Uppsala, Sweden

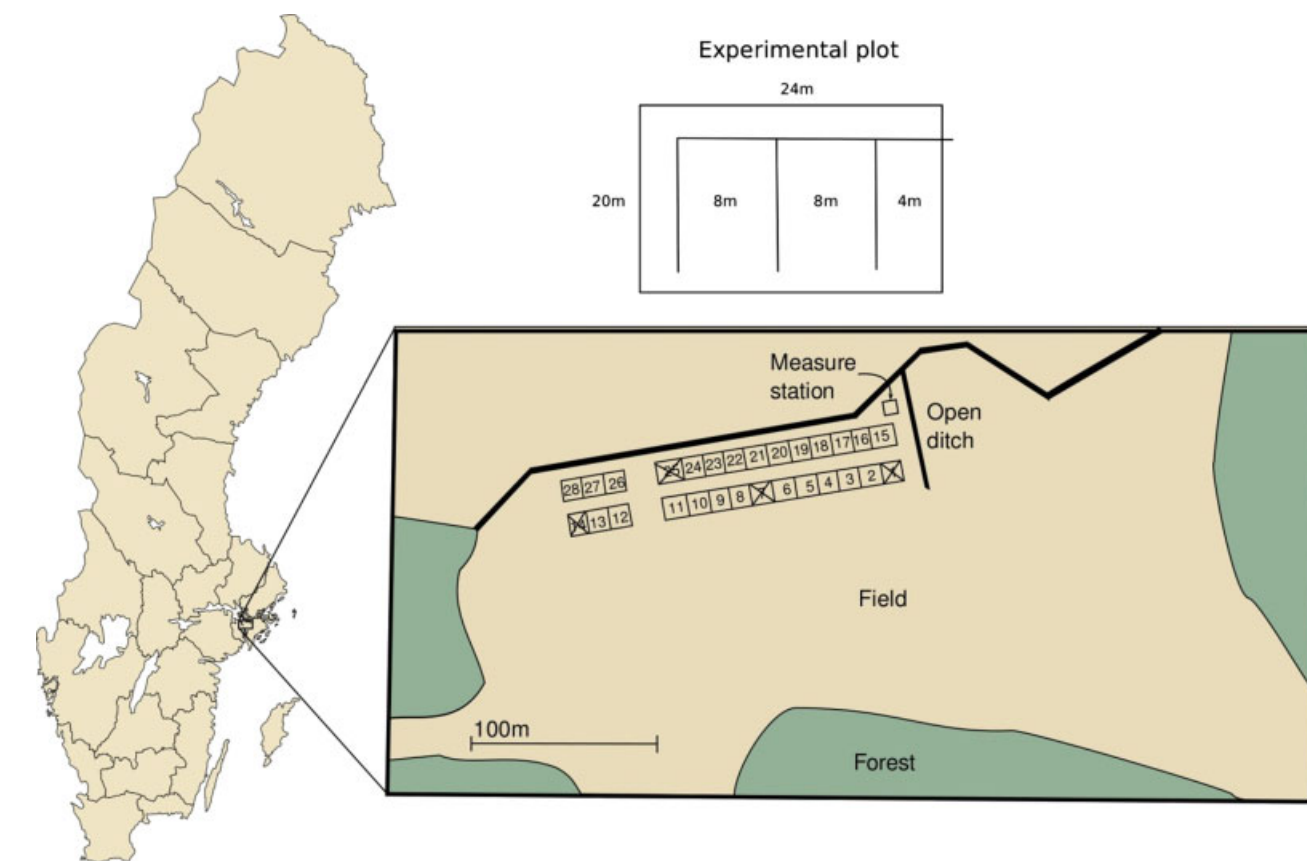


Figure 1. Map of Sweden and the location of the experimental site with drained plots and recipient ditch in the centre of the flat valley. All plots except numbers 1, 7 14 and 25 (unfertilised fallow) were included in the study. Water sampling took place in a measuring basement situated close to the northwest corner of plot 15.

approximately 10 cm wide and 10–20 cm high of prismatic shape. Large vertical pores (up to 5 mm wide) are apparent between the aggregates, especially in the subsoil, and abundant fine pores run in old root channels. Frequent precipitation of iron oxides can be seen in root channels, on aggregate walls and as 3 mm diameter patches unevenly distributed within the soil. Under wet conditions the aggregates are easily destroyed by digging. Soil pH and total organic carbon (OC) content are given in Table 1. There were no significant differences ($P > 0.05$) in soil pH and OC between treatments. One year after drainage, just before the experiment started in 2007, the mean topsoil OC was 2.5%, with a coefficient of variation of less than 17% between all included plots. The clay, silt and sand contents in the topsoil and the upper subsoil were about 60, 30 and 10%, respectively for all plots. In the deeper

subsoil (70–100 cm depth) the corresponding data were 54, 34 and 12%. At that depth the bulk density was low and the organic matter was low in nitrogen. This is typical for similar soils¹⁰ and indicative of crack formation stabilised by old organic matter. The dominating clay mineral is illite. Kaolinite is also present in smaller quantities.

2.1 Pesticide leaching

We studied the leaching of seven different pesticides with contrasting properties¹¹ (Table 2). It should be noted that both pesticide half-lives and adsorption partitioning coefficients are dependent on soil properties and the values presented in Table 2 may, therefore, not be representative for the clay soil at this site. Pesticide leaching was studied in two different crop rotations (Table 3),

Table 1. Mean values and standard deviations (SD) of soil pH and concentrations (%) of organic carbon (OC) at the start of the project in the autumn of 2007 and five years later in the spring of 2012 after repeated different tillage treatments and after structure liming first year

Sampling time	Property	Depth (cm)	Shallow tillage		Structure-limed		Conventional ploughing	
			Mean	SD	Mean	SD	Mean	SD
2007	pH	0–2	6.4	0.2	6.3	0.1	6.4	0.1
2012	pH	0–2	6.1	0.2	6.5	0.5	6.1	0.1
2007	OC (%)	0–23	2.4	0.5	2.5	0.5	2.5	0.5
2007	OC (%)	23–60	1.4	0.3	1.5	0.4	1.5	0.3
2007	OC (%)	60–90	0.6	0.1	0.6	0.1	0.6	0.1
2012	OC (%)	0–2	2.7	0.2	2.7	0.3	2.6	0.3

Table 2. Herbicide properties and leaching potential data taken from the Pesticide Properties Database (PPDB, 2010)¹¹

Substance	DT ₅₀ lab ^a (days)	DT ₅₀ field ^b (days)	K _{oc} ^c (cm ³ g ⁻¹)	GUS ^d	pK _a ^e
Bentazone	13	14	55.3	2.30	3.28
MCPA	24	25	74 ^f	2.94	3.73
Fluroxypyr	1	51	195 ^f	0	2.94
Clopyralid	34	11	5.0	5.06	2.01
Glyphosate	12	12	1435	-0.49	2.34
Thifensulfuron-methyl	4	4	28.3	1.53	4.4
Tribenuron-methyl	14	14	35	2.88	4.7

^a Degradation half-life for aerobic conditions measured in the laboratory.^b Degradation half-life for aerobic conditions measured in the field.^c Adsorption distribution coefficient to organic carbon.^d Groundwater ubiquity score.^e Acid dissociation constant.^f Freundlich adsorption coefficient to organic carbon.**Table 3.** Year, crop, date and commercial brand name of herbicides applied in 2008–2011 in crop rotations I and II (number of conventionally ploughed plots/total number of treated plots)

Year	Rotation I		Herbicide (16/20 plots)	Rotation II		Herbicide (4/4 plots)
	Crop	Date		Crop	Date	
2008	Spring barley	24/4	Glypro Bio ^{a, b}	Winter wheat	26/6	Harmony 50T Plus ^c
	Spring barley	26/6	Harmony 50T Plus ^c	After W wheat	16/8	Glypro Bio ^b
2009	Spring barley	9/6	Ariane S ^d	Winter wheat	6/5	Harmony 50T Plus ^c
2010	Oats	23/6	Ariane S ^d	Oats	23/6	Ariane S ^d
	Oats	22/9	Glypro Bio ^b	After oats	22/9	Glypro Bio ^b
2011	Pea	11/6	Basagran ^e	Pea	11/6	Basagran ^e

^a Only in eight shallow-tilled plots.^b Active ingredient glyphosate (49%).^c Active ingredients thifensulfuron-methyl (37%) and tribenuron-methyl (17%).^d Active ingredients MCPA (20%), fluroxypyr (4%) and clopyralid (2%).^e Active ingredient bentazone (87%).

both with oats and peas during the last two years (2010–2011). In crop rotation I (20 plots), conventional autumn ploughing was compared with shallow autumn tillage and the effects of previous structure-liming in autumn 2007⁹ were examined. Glyphosate was applied before sowing in spring 2008 to control couchgrass in eight shallow-tilled plots in crop rotation I (Table 4). In early summer the same year, the low-dose substances thifensulfuron-methyl and tribenuron-methyl were applied in both rotations. In autumn 2008 glyphosate was applied after harvest (four plots) in crop rotation II in order to control couchgrass and volunteer cereals. The three pesticides clopyralid, fluroxypyr and MCPA (all ingredients in the same commercial product) were sprayed for weed control on 9 June 2009 in crop rotation I (20 plots) and on 23 June 2010 in both rotations (24 plots). Glyphosate was applied after harvest in September 2010 and bentazone was applied on 11 June 2011 in both rotations (24 plots). Most applications were made in the evening, with no wind and always in the recommended dose. The total loads of herbicides applied (Table 4) were similar to those reported from agricultural catchments within the Swedish National Pesticide Monitoring Programme.^{12,13} Precipitation was measured at the site with unheated tilting bucket equipment and collected in a data logger. Since snow amounts are easily underestimated with this equipment, the snow cover was recorded manually (five days a week) on an open field at the Norsborg drinking water

treatment plant situated 6 km northeast of the experimental site. Snow accumulation between melting periods was estimated from these data.

2.2 Water sampling and analysis

Water discharge from each plot was measured with tilting vessels in an underground basement where sampling of drainage water also took place. The water was sampled flow-proportionally, with every subsample representing 0.003 mm discharge in summer and 0.04 mm discharge in the rest of the year. The bulk samples were collected weekly (or for the first flow events following application more frequently). Accordingly, the actual peak concentrations were not captured. Immediately after collection all samples were frozen and sent to the Organic Risk Pollutants Laboratory, Department of Aquatic Sciences and Assessment, SLU, where they were analysed when detectable concentrations of herbicides were expected.

The concentration of thifensulfuron-methyl and tribenuron-methyl (in 2008) was determined with solid-phase extraction followed by liquid chromatography and mass spectrometry (LC-MS) and the concentration of clopyralid, fluroxypyr and MCPA (in 2009) by the same solid-phase extraction and by derivatisation and gas chromatography/mass spectrometry (GC/MS).¹⁴ Fluroxypyr and MCPA (in 2010) and bentazone (in 2011) were analysed by mass

Table 4. Year, date of application, substance analysed in drainage water, crop and applied dose of detected substance, together with the general dose (in g ha^{-1}) applied in Swedish monitored small catchments in 2008–2011

Year	Date	Substance	Crop	Dose (g ha^{-1})	General dose (g ha^{-1})
2008	24/4	Glyphosate	Before barley	707	748
2008	26/4	Thifensulfuron-methyl	Spring barley	4	6
		Tribenuron-methyl	Spring barley	2	3
2008	16/8	Glyphosate	After winter wheat	1060	1116
2009	26/5	Thifensulfuron-methyl	Winter wheat	6	6
		Tribenuron-methyl	Winter wheat	3	3
2009	9/6	Clopyralid	Spring barley	52	48
		Fluroxypyr	Spring barley	104	81
		MCPA	Spring barley	520	590
2010	23/6	Fluroxypyr	Oats	104	75
		MCPA	Oats	520	510
		Glyphosate	After oats	1060	1110
2011	11/6	Bentazone	Pea	475	500

spectrometric determination (LC-MS/MS).¹⁵ Dissolved glyphosate (DissGly) and its main metabolite AMPA were analysed in winter 2008/2009 and 2010/2011, which involved ion exchange and derivatisation, followed by final identification and quantification by GC/MS. In winter 2010/2011, glyphosate analysis included particulate glyphosate (PartGly), which was trapped using a cellulose acetate filter with pore size $0.45 \mu\text{m}$. Glyphosate results have been presented earlier, together with a complete description of the analytical procedure.⁹ The median value for limit of detection (LOD; in $\mu\text{g L}^{-1}$) was: 0.003 for bentazone, 0.005 for clopyralid, 0.01 for fluroxypyr, 0.003 for MCPA, 0.006 for thifensulfuron-methyl and tribenuron-methyl, 0.03 for dissolved glyphosate, 0.1 for particulate glyphosate and 0.2 for AMPA. Measured concentrations were below the LOD values for dissolved glyphosate, particulate glyphosate and AMPA in 20, 22 and 45% of the samples, respectively. Dissolved reactive phosphorus (DRP) and particulate phosphorus (PP) were determined⁹ for all samples which were analysed for any pesticides.

3 RESULTS AND DISCUSSION

3.1 Precipitation and discharge

Drainage was highly efficient and practically all winter precipitation was discharged through the subsurface drains. The ratio between precipitation and discharge was higher than average in June 2011 and much higher in June 2009 (Table 5). In August and September 2010, this ratio was more than four times higher than the average. Eastern Sweden typically experiences frequent early summer drought,¹⁶ but in the present study repeated summer rainfall occurred in mid-June 2009 (12 mm, 4 mm and 46 mm on 12, 13 and 14 June, respectively), with a maximum intensity of 9 mm h^{-1} on 14 June. This was followed by a pronounced water discharge peak (Figure 2b) of 40 mm lasting for two days (15–16 June), which was collected as a first composite sample. A sharp decline in water flow followed and a second composite sample six days later represented 5 mm discharge. In contrast, the growing season of 2010 was characterised by a dry June and first half of July, followed by three repeated rainstorms of escalating intensity

Table 5. Monthly precipitation (Prec) and total snow accumulation (Snow acc) in winter periods (October–April current year and January–April following year), water discharge (Flow) and ratio Flow/Prec for the experimental years and long-term (1988–2011) average

Year		May	June	July	August	September	October–April	Snow acc (cm)
2008	Prec (mm)	30	5	44	42	8	385	14
	Flow (mm)	10	1	0	4	5	395	
	Flow/Prec	0.33	0.20	0	0.03	0.63	0.99	
2009	Prec (mm)	45	95 ^a	94	54	35	384	50
	Flow (mm)	3	43	3	1	0	370	
	Flow/Prec	0.07	0.45	0.03	0.02	0	0.85	
2010	Prec (mm)	53	39	155 ^b	95	51	290	75
	Flow (mm)	16	3	8	87	42	310	
	Flow/Prec	0.30	0.08	0.05	0.92	0.82	0.85	
2011	Prec (mm)	40	70	26	138	72	358	3
	Flow (mm)	3	14	0	0	4	350	
	Flow/Prec	0.08	0.20	0	0	0.06	0.96	
1988–2011	Prec (mm)	40	67	82	69	63	338	32
	Flow (mm)	7	12	2	18	10	360	
	Flow/Prec	0.15	0.18	0.02	0.21	0.16	0.97	

^a Maximum intensity 46 mm day^{-1} in the middle of the month.

^b Maximum intensity 79 mm day^{-1} at the end of the month.

in late July–early August (29 mm, 43 mm, 79 mm and 21 mm on 24, 25 and 27 July and 2 August, respectively). Repeated rain events of such magnitude only occur every 10 years in this region.¹⁶ This rain storm resulted in complete flooding of the measuring basement on 29–31 July 2010 which destroyed the samples from this event. A water sample which represented 6 mm discharge was taken on 3 August after the peak flow (> 25 mm) had passed. On 23 June 2011, 17 mm rain fell within two hours on soil that was already wet from 5 mm rain two days earlier. This resulted in 8 mm and 4 mm water discharge on the following two days. This was collected and analysed for bentazone, which was applied 12 days earlier. The two winters following autumn application of glyphosate (2008/2009, 2010/2011) differed. The autumn of 2008 was warm and most winter discharge occurred in October–December (Figure 2a), while winter 2010/2011 was cold, with substantial accumulation of snow and major drain discharge occurring in spring 2011 (Figure 2c). Water discharge between the different plots had a mean coefficient of variation of 22% in summer and 25% in winter.

3.2 Concentrations of pesticides in drain water

The sulphonylureas (thifensulfuron-methyl and tribenuron-methyl) were not detected above LOD in 2008. Because of the fast dissipation of these substances,¹⁷ they were not analysed for in subsequent years. Unlike these low-dose substances, detectable levels of all other herbicides were found every year in drain flow in the first 1–2 months after early summer application. Detectable concentrations of fluroxypyr and MCPA were also observed 31 days after application (Table 6) in the samples taken after flooding of the measuring station. Detection of pesticides in the first few rainfall/drainage events after application is consistent with the preferential flow concept.^{2,18} Another indication of preferential flow was the simultaneous arrival of clopyralid and fluroxypyr on 14–16 June 2009, despite large differences in K_{oc} values (Table 2). However, since only five days had passed between application and rainfall, the substances might not have been in equilibrium with the soil solid material due to slow kinetics.¹⁹ Dissolved glyphosate was detected in consecutive events in autumn 2008. Both particle-bound glyphosate and dissolved glyphosate were

detected in the discharge from all fast-flow events in autumn 2010. Swedish guideline values based on predicted no effects ($C_{no\ effect}$) on surface water ecosystems have been estimated for a number of pesticides by the Swedish Chemicals Agency.^{20,21} Levels above the $C_{no\ effect}$ concentrations were observed in 50% of the plots for MCPA and in 33% for bentazone (Table 6). Levels of glyphosate, AMPA, clopyralid and fluroxypyr were on all occasions below their $C_{no\ effect}$ concentrations. After the peak concentration on 14–16 June 2009, subsequent concentrations of clopyralid, fluroxypyr and MCPA decreased by 63, 55 and 38 % of the peak values as water flow continued more slowly in the following six days. These relatively fast declines demonstrate that the leaching was event-driven. High concentrations of bentazone (up to $63\ \mu\text{g L}^{-1}$) after one short but extremely intensive rain episode in June 2011 supports the general conclusion that pesticide concentrations may largely be determined by the intensity of rainfall events rather than their duration for soils prone to preferential flow.²²

The coefficient of variation in the most important leaching event for the substances studied varied between 72 and 115% between all different plots (including different treatments) and increased in the order bentazone < clopyralid < fluroxypyr < PartGly < MCPA < DissGly. These highly variable pesticide concentrations were not significantly correlated to the basic soil factors pH value, clay content and organic matter content in the topsoil, which only showed minor variance (2, 17 and 10%, respectively).

3.3 Leaching losses of pesticides

The amount of pesticide leached in summer periods from conventionally ploughed plots sprayed simultaneously with the same herbicide in 2009–2011 varied between 0.2 and $3.3\ \text{g ha}^{-1}$ (0.1–1.6% of amount applied) (Table 7). Tile-drain losses in this range have been reported from other single experimental sites²³ and from critical source areas in catchments.²⁴ Leaching losses above 1% are generally associated with large rainfall amounts shortly after application.²⁵ However, for our case the hydrological conditions did not represent 'worst-case' leaching conditions and hence the large leaching losses demonstrate the great potential for preferential transport in this soil. Losses exceeding 0.1% took

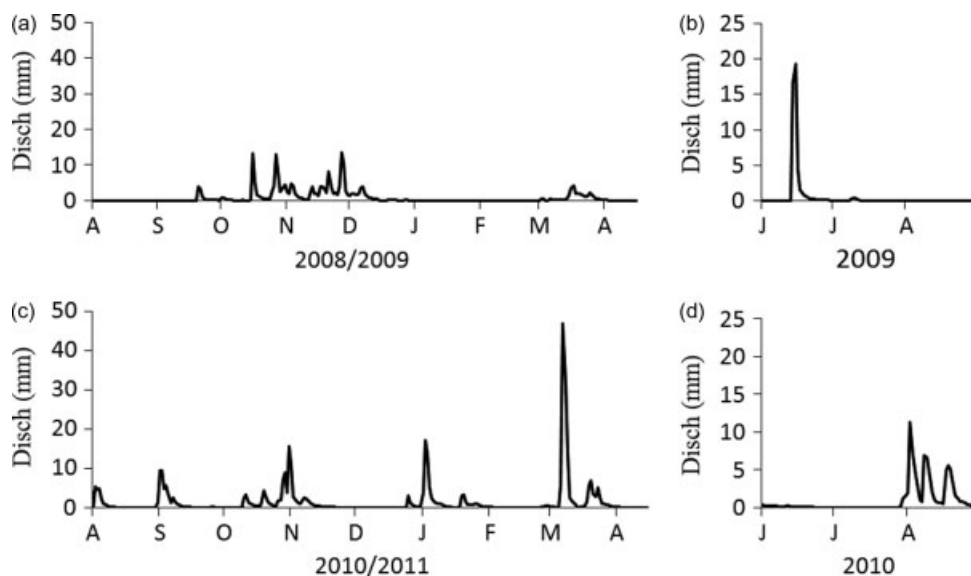


Figure 2. Water discharge (in mm day^{-1}) in winter periods following application of glyphosate and in summer periods following application of clopyralid, fluroxypyr and bentazone.

Table 6. Year, date of application of substance (including glyphosate metabolite AMPA) and glyphosate in dissolved (diss) form and total glyphosate, numbers of plots (Plots), number of days (No. days) until major rain event, Swedish guideline values for no effect ($C_{no\ effect}$), maximum (Max) and mean concentration in the main drainage event, ratio of number of plots with concentration exceeding $C_{no\ effect}$ to total number of plots treated (Ratio $C_{no\ effect}$) and total period (days) after application when values exceeding $C_{no\ effect}$ were detected

Year	Date	Substance	No. days	$C_{no\ effect}$ ($\mu\text{g L}^{-1}$)	Maximum ($\mu\text{g L}^{-1}$)	Mean ($\mu\text{g L}^{-1}$)	Ratio $C_{no\ effect}$	Period (days)
2008	16/8	Glyphosate diss.	47	100	1.2	0.48	0/4	—
		AMPA	47	500	0.3	—	—	—
2009	9/6	Clopyralid	5	50	5.5	2.2	0/20	—
		Fluroxypyr	5	100	1.7	0.67	0/20	—
		MCPA	5	1	5.5	2.0	10/20	5–14
2010	23/6	Fluroxypyr ^a	31	100	0.3	0.081	0/24	—
		MCPA ^b	31	1	0.04	0.007	0/24	—
2010	22/9	Glyphosate diss.	33	100	3.9	0.58	0/24	—
		Glyphosate total	33	100	9.4	2.2	0/24	—
		AMPA	33	500	0.7	—	—	—
2011	11/6	Bentazone	12	30	63	23.9	8/24	12–16

^a Generally only analysed in dissolved form.

^b Late collection of sample, as the measuring station was flooded.

place from 22 to 24 plots (92–100% of the experimental area) for clopyralid and bentazone, while the relative losses of MCPA exceeding 0.1% represented 42% of the area. According to a recent review of pesticide losses through tile drains, relative losses exceeding 0.1% occurred from 43% of the sites in Europe, while in the United States the corresponding figure was 59%.¹

Since we did not measure pesticide sorption and degradation, we discuss leaching in relation to the pesticide properties given in the Pesticide Properties Database.¹¹ The relative leaching losses of the substances studied here are presented in Table 7. Leaching of clopyralid (1.62%), which is the substance with the highest GUS index, was much greater than that of fluroxypyr (0.22%) and MCPA (0.14%), which were applied at the same time. Based on the GUS index for fluroxypyr and MCPA (Table 2), leaching of fluroxypyr was unexpectedly high. Since the GUS index for these substances was calculated from DT_{50} values measured in the laboratory, this may be explained by the much slower degradation measured under field conditions. The losses of bentazone represented 0.70% of the amount applied (June 2011) and the losses of total glyphosate 0.16% of the amount applied (in winter 2010/2011).

These significant losses are in contrast to the small GUS index values of these substances (Table 2) and, hence, indicate preferential transport. Based on the GUS index for MCPA, it can be expected to leach more than bentazone. However, the relative losses of bentazone in this study (0.70%) considerably exceeded the losses of MCPA (0.14%) two years earlier, demonstrating the importance of hydrological conditions for leaching of these pesticides. Surprisingly, autumn application of glyphosate in 2008 and 2010 resulted in quite similar losses in dissolved form in the following winters (0.9 g ha⁻¹ corresponding to 0.08% of applied amounts; Table 7), irrespective of whether the main discharge took place after autumn rain followed by a mild winter (2008) or in connection with snowmelt after a cold winter with continuous snow cover (2011). In laboratory experiments conducted at the same average temperature, significantly less glyphosate degradation has been reported under constant freezing conditions compared with at fluctuating temperatures with repeated freezing–thawing cycles.²⁶ Due to slow degradation during the winter of 2010/2011 owing to long-lasting snow cover, glyphosate was available for

Table 7. Year, date, applied substance, including the sum of the three components in the commercial product Ariane S, mean losses from all ploughed plots with standard deviation (SD), mean losses relative to applied amount, range of the relative losses and area with relative losses exceeding 0.1 g ha⁻¹. Glyphosate was analysed in both dissolved (diss.) and particulate (part.) form in 2010

Year	Date	Substance	Mean (g ha ⁻¹)	SD	Relative losses (%)	Range of relative losses (%)	Area (%)
2008	16/8	Glyphosate diss.	0.89	0.64	0.084	0.02–0.17	25
2009	9/6	Clopyralid	0.84	0.70	1.62 ^c	0.09–4.55	92
		Fluroxypyr	0.24	0.36	0.22	0.002–0.96	60
		MCPA	0.71	0.89	0.14	0.003–0.49	42
		Sum	1.81	3.03	0.34	0.02–1.36	60
2010	23/6	Fluroxypyr ^a	> 0.03	0.02	> 0.03	—	—
2010	22/9	Glyphosate diss. ^b	0.90	0.32	0.085	0.05–0.12	—
		Glyphosate part.	0.82	0.25	0.064	0.08–0.10	—
		Glyphosate total	1.72	1.47	0.15	0.12–0.23	100
2011	11/6	Bentazone	3.31	2.92	0.70 ^b	0.42–2.16	100

^a From late sample after flooding of the measuring station.

^b Period 22 September–15 April and calculated from the same four plots as treated in 2008.

^c Relative losses of clopyralid were significantly greater ($P < 0.01$) than losses of fluroxypyr applied simultaneously.

leaching during the main snowmelt event, which was fast and probably resulted in preferential transport.

3.4 Herbicide correlation with particulate phosphorus and plot position

In spite of the small variation in the amounts of water discharge between plots, there was a large variation in herbicide losses for all substances resulting from the highly varying concentrations in drainage water. In addition, the concentrations of clopyralid, bentazone, MCPA and fluroxypyr were all significantly correlated to the particle-bound phosphorus (PP) concentrations from the same plot (Figure 3). Similar relationships have previously been reported between total glyphosate and PP for the same field.⁹ Due to their strong sorption, both glyphosate and PP are considered to leach mainly through preferential transport in macropores.^{18,27,28} Our results suggest that preferential transport dominates leaching also for the weakly sorbed substances at this site. In addition, since the pesticides which were applied at the soil surface were leaching with a similar pattern as PP, this suggests that the topsoil was the major source of leached PP.

We did not observe any surface runoff in the direction of the recipient ditch during the experimental period. Lateral flows below the soil surface and e.g. on a plough pan were also unlikely to occur, since there was no distinct plough pan at the site. There was no correlation between the topsoil (0–23 cm) pH and the plot position. However, topsoil OC clearly increased with decreasing distance between plot mid-point and the recipient ditch ($R^2 = 0.70\%$, $P < 0.001$) and pH in the deeper subsoil (60–90 cm) decreased ($R^2 = 78\%$, $P < 0.001$). The concentration of all pesticides tended to increase with decreasing distance between plot position and the recipient ditch. The relationship was significant for bentazone, and was also significant from a total ranking of all pesticides

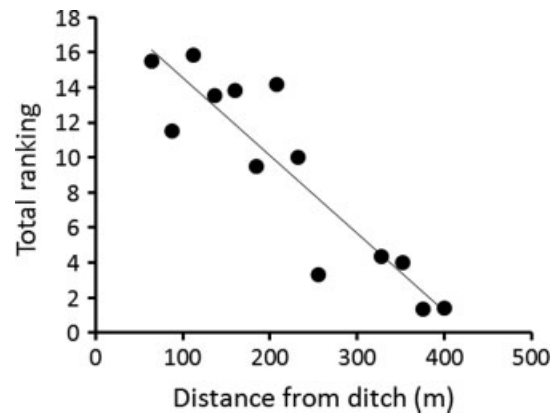


Figure 4. Total ranking of mean concentration of clopyralid, fluroxypyr, MCPA, bentazone, dissolved glyphosate and particulate glyphosate related to the distance between the ditch and the centre of the respective plot. The estimates were made for the observed concentrations in the major event for every substance. The slope of the regression line is significantly different from zero ($P < 0.001$).

detected (Figure 4). The reason for the gradient in herbicide concentrations with distance from the ditch is not clear. Based on the (randomised) position of plots with different soil management regimes, the concentrations of e.g. bentazone might have been slightly overestimated from shallow-cultivated plots, and slightly underestimated from structure-limed plots, since the slope of the regression line between soil management and distance was not equal to zero (Figure 5). This effect (up to 3%) was corrected for when comparing leaching of all detected substances (Table 8), based on the relationship between concentration of the substance and the position of the plot.

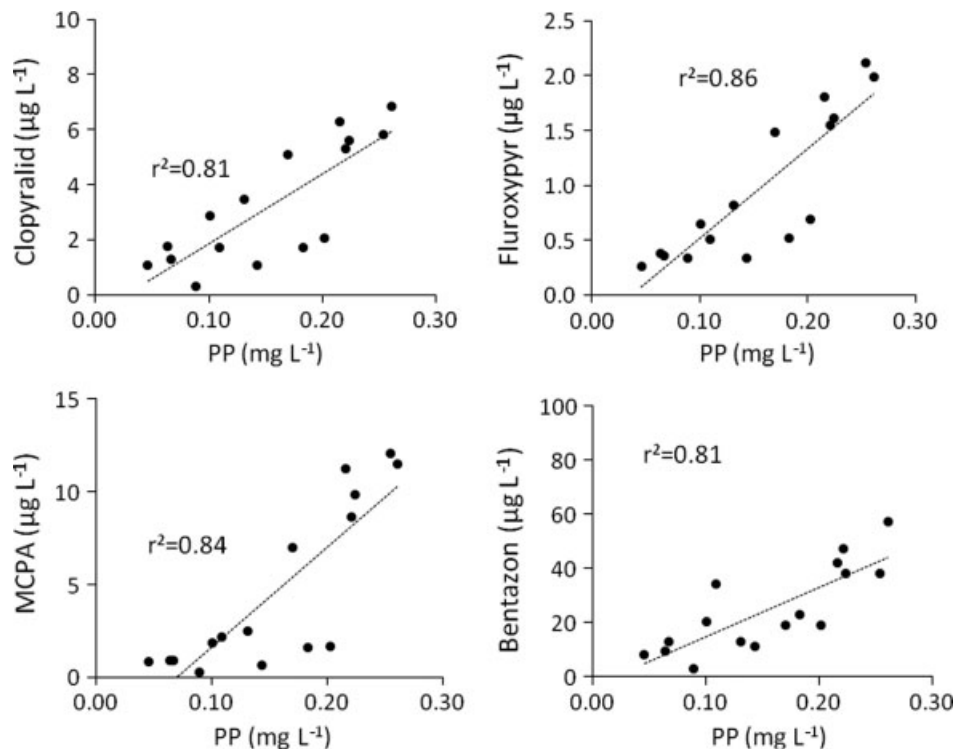


Figure 3. Concentrations of clopyralid, bentazone, MCPA and fluroxypyr related to particulate phosphorus (PP) (including correlation coefficient r^2) in water draining from different plots during periods of maximum detected concentrations.

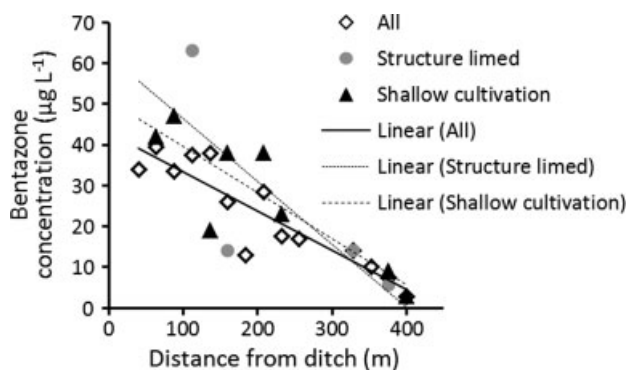


Figure 5. Concentration of bentazone as a function of distance to the recipient ditch. Regression lines are based on concentration from shallow-cultivated plots and structure-limed plots, and compared with all plots, including conventionally ploughed plots. The slope of the regression line is significantly different from zero ($P < 0.001$).

3.5 Effects of soil management, soil structure, pH and organic matter

There was a general tendency for larger losses of all substances from shallow-tilled plots than from ploughed plots, with or without previous structure liming (Table 8). The apparent differences, which were not significant for any single substance, increased in the order clopyralid < MCPA < bentazone < fluroxypyr < total glyphosate. However, estimated for all five substances lumped together (paired *t*-test), the difference between shallow-tilled and ploughed structure-limed plots was significant ($P < 0.05$), both before and after adjustment to the effect of plot position in relation to the ditch. From soils where preferential flow and transport are important, ploughing is generally considered to reduce pesticide leaching by interrupting continuous macropores.^{29–32} For our case the larger losses from the shallow-tilled plots may also have been an effect of shallow and uneven accumulation of crop residues in these plots which resulted in uneven infiltration and preferential herbicide transport along straw residues.³³

At the study site, it has been demonstrated that structure liming (quicklime) significantly improves soil aggregate stability measured as a decrease in readily dispersed clay.⁹ Improved aggregate stability should influence the transport of glyphosate which adsorbs strongly to clay particles. However, the improved aggregate stability did not result in any significantly smaller losses of glyphosate from structure limed plots compared to conventionally tilled plots.

Structure liming causes clay colloids in the topsoil to form a ‘card-house’ pattern.³⁴ This may theoretically result in a more spatially uniform infiltration in the uppermost topsoil which moderates preferential flow. However, the improved aggregate stability and other changes in the topsoil that may follow from any changed particle organisation did not result in significantly smaller losses of glyphosate from structure limed plots compared to conventionally tilled plots.

For ionisable pesticides, leaching is also affected by soil pH,³⁵ with weaker sorption at higher pH. Based on the pK_a values of the substances studied here and the small differences in pH between treatments (Table 8), any pH effects on leaching were probably minor. The topsoil OC content is often higher under long-term shallow tillage than under conventional tillage, which has consequences for pesticide sorption and degradation.³¹ However, in our case the OC content was not significantly different between treatments and there were no significant differences in subsoil OC between plots with different management regimes.

The generally low bulk density of the subsoil may be a result from the existence of many cracks. However, the highly variable leaching of all pesticides between different plots was possibly the result of varying frequency and shape of the cracks in these lower soil layers. Both ‘gyttja’ (cohesive old matter of organic origin settled in marine or lake sediment) and oxidised iron (rust) have been frequently observed in the lower soil layer. Such material might strengthen the crack walls and make them into permanent pathways, especially in the deeper layer with low pH close to the ditch in the centre of the flat valley. Corresponding channels, especially those in direct contact with drains, can serve as effective transport pathways for pesticides³² and for PP.³⁶ The coefficient of variation in relative leaching losses between all substances for the shallow-tilled plots varied between 40 and 92%. The coefficient of variation in the relative leaching losses from all plots and for all substances combined (92–156%) varied even more. In conclusion, the variation in relative leaching losses between plots within the same treatment was larger than that between different substances. This finding also demonstrates that the differences in transport pathways through the soil between plots have a larger effect on pesticide concentrations than the differences in pesticide properties.

4 CONCLUSIONS

Concentrations of the herbicides bentazone, clopyralid, fluroxypyr, MCPA and glyphosate were measured in subsurface drain

Table 8. Year of application, mean and standard deviation (SD) of transported masses of the applied substances (in $g\ ha^{-1}$) from tilled, structure-limed (+ ploughed) and conventionally ploughed plots

Year	Substance	Shallow tillage			Structure-limed			Conventional ploughing		
		Un-adjusted	Adjusted	SD	Un-adjusted	Adjusted	SD	Un-adjusted	Adjusted	SD
2009	Clopyralid	1.16	1.14	0.77	1.07	1.13	0.95	0.73	0.71	0.59
2009	Fluroxypyr	0.36	0.35	0.29	0.25	0.26	0.28	0.22	0.21	0.25
2009	MCPA	1.11	1.09	1.03	0.86	0.88	1.25	0.63	0.61	0.82
2011	Bentazone	4.78	4.73	2.84	3.52	3.75	3.81	3.40	3.32	2.53
2010	Glyphosate ^a	3.81	3.77	2.58	0.85	0.90	1.13	1.59	1.56	1.56

Note: Mean transported losses are given both as unadjusted values and values adjusted for the distance to the ditch.

^a Total glyphosate in both particulate and dissolved form in the period 22 September 2010 – 15 April 2011.

discharge from a clay field during a four-year study. Despite hydrological conditions not representing a worst case scenario for leaching, the relative leaching losses of all herbicides studied were large compared to values reported in the literature. Measured concentrations of bentazone and MCPA exceeded Swedish guideline values based on predicted no effect on aquatic ecosystems for 50 and 33% of the plots for MCPA and bentazone, respectively. All substances studied (except sulphonylureas which were not detected), irrespective of sorption strength, showed similar leaching patterns. These observations clearly demonstrate that preferential transport in macropores is the dominant transport process at this site. The variation in relative leaching losses between plots within the same treatment was greater than that between different substances. Crack stabilisation by gyttja, especially in the deeper subsoil, was suggested as an important explanatory factor for this large spatial variation in pesticide leaching, although it was not possible to investigate differences in gyttja content between plots. Continuous macropores connecting the soil surface to the subsoil may be a factor contributing to the generally large pesticide losses observed after shallow tillage. However, careful studies of soil macropore systems, including topsoil and subsoil properties, are needed to explain the unpredictability in leaching at this site.

ACKNOWLEDGEMENTS

Sincerest thanks to Stockholm Water Co, which funded the majority of the experimental field equipment, and to the Society for Rural Economy and Development for fruitful cooperation. Special thanks to Nils-Erik Stackhammar, who managed the experiment, and to Johan Frank of Stockholm Water Co, who took most of the water samples. Thanks also to Gunborg Alex, Eva Lundgren, Åsa Ramberg and Mårit Petersson at the Organic Risk Pollution Laboratory for good analytical work. The study was funded by the Swedish Farmers Foundation (SLF), which is gratefully acknowledged.

REFERENCES

- Brown CD and Van Beinum W, Pesticide transport via subsurface drains in Europe. *Environmental Pollution* **157**:3314–3324 (2009).
- Kladivko EJ, Brown L and Baker J, Pesticide transport to subsurface tile drains in humid regions of North America. *Critical Reviews in Environmental Science and Technology* **31**:1–62 (2001).
- Brown CD, Hodgkinson A, Rose DA, Syers J and Wilcockson SJ, Movement of pesticides to surface waters from a heavy clay soil. *Pesticide Sciences* **43**:131–140 (1995).
- Riise G, Lundekvam H, Wu QL, Haugen LE and Mulder J, Loss of pesticides from agricultural fields in SE Norway – runoff through surface and drainage water. *Environmental Geochemistry and Health* **26**:269–276 (2004).
- Gustafson DI, *Pesticides in Drinking Water*. Van Nostrand Reinhold, New York (1993).
- Leu C, Singer H, Stamm C, Müller SR and Schwarzenbach RP, Variability of herbicide losses from 13 fields to surface water within a small catchment after controlled herbicide application. *Environmental Science and Technology* **38**:3835–3841 (2004).
- Doppler T, Camenzuli L, Hirzel G, Krauss M, Lück A and Stamm C, Spatial variability of herbicide mobilisation and transport at catchment scale: insight from a field experiment. *Hydrology and Earth System Sciences* **16**:1947–1967 (2012).
- Flury M, Flüher H, Jury WA and Leuenberger J, Susceptibility of soils to preferential flow of water: a field study. *Water Resources Research* **20**:1945–1994 (1994).
- Ulén B, Alex G, Kreuger J, Svanbäck A and Etana A, Particulate-facilitated leaching of glyphosate and phosphorus from a marine clay soil via tile drains. *Acta Agriculturae Scandinavica B: Soil and Plant* **62**(Suppl. 2):217–228 (2012).
- Kirchmann H, Properties and classification of soils of the Swedish long-term fertility experiments. I. Sites at Fors and Kungsängen. *Acta Agriculturae Scandinavica B: Soil and Plant* **39**:361–371 (1991).
- PPDB Pesticide Properties Database. EU-project Footprint Pesticide database updated 6 August (2010). Available: <http://www.eu-footprint.org/ppdb.html>
- Graaf S, Adielsson S and Kreuger J, Resultat från miljöövervakningen av bekämpningsmedel (växtskyddsmedel) – Årssammanställning 2009 [Results from environmental monitoring of pesticides – annual report 2009], *Ekohydrologi* **120**. Department of Soil and Environment, Swedish University of Agricultural Sciences, Valsåtra-Ultuna, 56 pp. (2010).
- Graaf S, Adielsson S and Kreuger J, Resultat från miljöövervakningen av bekämpningsmedel (växtskyddsmedel) – Årssammanställning 2010 [Results from environmental monitoring of pesticides – compilation year 2010], *Ekohydrologi* **128**. Department of Soil and Environment, Swedish University of Agricultural Sciences, Valsåtra-Ultuna, 73 pp. (2011).
- Åkerblom M, Thorén L and Staffas A, Bestämning av bekämpningsmedel i dricksvatten. [Determination of pesticides in drinking water]. *Vår Föda* **42**:236–243 (In Swedish, with English abstract) (1990).
- Jansson C and Kreuger J, Multiresidue analysis of 95 pesticides at low nanogram/liter levels in surface waters using online pre-concentration and high performance liquid chromatography/tandem mass spectrometry. *Journal of AOAC International* **93**:1732–1747 (2010).
- Wern L and German J, Korttidsnederbörd i Sverige 1995–2008 [Short term precipitation in Sweden 1995–2008], *Meteorologi* **139**. Swedish Meteorological and Hydrological Institute, Norrköping, 34 pp. (2009).
- Cessna AJ, Elliot JA and Bailay J, Leaching of three sulfonylurea herbicides during sprinkler irrigation. *Journal of Environmental Quality* **39**:365–374 (2009).
- Villholt KG, Jensen KH and Frederica J, Flow and transport processes in macroporous subsurface-drained glacial till soil I Field investigations. *Journal of Hydrology* **207**:98–120 (1998).
- Altfelder S, Streck T and Richter J, Nonsingular sorption of organic compounds in soil: the role of slow kinetics. *Journal of Environmental Quality* **29**:917–925 (2000).
- KEMI, *Guide Values for Plant Protection Products in Surface Waters* [online], Swedish Chemical Inspectorate (2010). Available: <http://www.kemi.se>
- Andersson M, Kreuger J, Preliminära riktvärden för växtskyddsmedel i ytvattnet, beräkning av riktvärden för 64 växtskyddsmedel som saknar svenskt riktvärde [Preliminary guideline values for pesticides in surface water of 64 substances lacking such Swedish values], Technical Report 144. Department of Soil and Environment, Swedish University of Agricultural Sciences, Valsåtra-Ultuna, 82 pp. (2011).
- Kördel W, Egli H and Klein M, Transport of pesticides via macropores. *Pure and Applied Chemistry* **80**:105–160 (2008).
- Accinelli C, Vicari A, Pisa PR and Catizone P, Losses of atrazine, metachlor, prosulfuron and triasulfuron in subsurface drain water: field results. *Agronomie* **22**:399–411 (2002).
- Freitas LG, Singer H, Müller SR, Schwarzenbach RP and Stamm C, Source area effects on herbicide losses to surface waters – A case study in the Swiss plateau. *Agriculture, Ecosystems and Environment* **128**:177–184 (2008).
- Flury M, Experimental evidence of transport of pesticides through field soils – a review. *Journal of Environmental Quality* **25**:25–45 (1996).
- Stenrød M, Eklo OM, Charnay MP and Benoit M, Effect of freezing and thawing on microbial activity and glyphosate degradation in two Norwegian soil. *Pesticide Management Science* **61**:887–898 (2005).
- Vereecken H, Mobility and leaching of glyphosate – a review. *Pesticide Management Science* **61**:1139–1151 (2005).
- Stamm C, Flüher H, Gächter R, Leuenberger J and Wunderli, H. Preferential transport of phosphorus in drained grassland soils. *Journal of Environmental Quality* **28**:515–522 (1998).
- Isensee AR, Nash RG and Helling CS, Effect of conventional vs. no-tillage on pesticide leaching to shallow groundwater. *Journal of Environmental Quality* **19**:434–440 (1990).
- Elliott JE, Machmer MM, Wilson LK and Henny CJ, Contaminants in ospreys from the Pacific northwest: II. Organochlorine pesticides,

- polychlorinated biphenyls and mercury, 1991–1997. *Archives of Environmental Contamination & Toxicology* **38**:93–106 (2000).
- 31 Larsbo M, Stenström J, Etana A, Börjesson E and Jarvis N, Herbicide sorption, degradation and leaching in three Swedish soils under long-term conventional and reduced tillage. *Soil and Tillage Research* **105**:200–208 (2009).
- 32 Jacobsen O and Kjær J, Is tile drainage water representative of root zone leaching of pesticides. Review. *Pesticide Management Science* **63**:417–428 (2007).
- 33 Kasteel R, Garnier P, Vachier P and Coquet Y, Dye tracer infiltration in the plough layer after straw incorporation. *Geoderma* **137**:360–369 (2007).
- 34 Koorevaar P, Menelik G, Dirksen C, Interaction between solid and liquid phases, in *Elements of Soil Physics*. Elsevier Science, Amsterdam, Chapter 1.4, pp. 21–25 (1982).
- 35 Wauchope RD, Yeh S, Linders JBHJ, Kloskowski R, Tanaka K, Rubin B, et al., Pesticide soil sorption parameters: theory, measurements, uses, limitations and reliability. *Pesticide Management Science* **58**:419–445 (2002).
- 36 Øygarden L, Kværner J and Jenssen PD, Soil erosion via preferential flow to drainage system in clay soils. *Geoderma* **76**:65–86 (1997).