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Particulate-facilitated leaching of glyphosate and phosphorus from a marine clay soil via tile drains

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Abstract

Leaching losses of autumn-applied glyphosate (1.06 kg ha^{-1}) via drainage water were examined by flow-proportional sampling of discharge from 20 drained plots in a field experiment in eastern Sweden. Samples were analysed for glyphosate in particulate-bound (PGly) and dissolved (DGly) form. The first 10 mm water discharge contained no detectable glyphosate but the following 70 mm had total glyphosate (TotGly) concentrations of up to 6 μg L^{-1}, with 62% occurring as PGly. On average, 0.7 g TotGly ha^{-1} was leached from conventionally ploughed plots compared with 1.7 g TotGly ha^{-1} from shallow-tilled plots (cultivator to 12 cm working depth). Higher glyphosate losses occurred in snowmelt periods in spring, but with the majority (60%) as DGly. All autumn concentrations of PGly in drainage water were significantly correlated ($p<0.001$) to the concentrations of particulate-bound phosphorus (PP) lost from the different plots (Pearson correlation coefficient 0.84), while PP concentrations were in turn significantly correlated to water turbidity (Pearson correlation coefficient 0.81). Leaching losses of TotGly were significantly lower (by 1.3 g ha^{-1}; $p<0.01$) from plots that had been structure-limed three years previously and ploughed thereafter than from shallow-tilled plots. Turbidity and PP concentration also tended to be lowest in discharge from structure-limed plots and highest from shallow-tilled plots. This difference in TotGly leaching between soil management regimes could not be explained by differences in measured pH in drainage water or amount of discharge. However, previously structure-limed plots had significantly better aggregate stability, measured as readily dispersed clay (RDC), than unlimed plots.

Key words: *glyphosate, drainage water, particulate phosphorus, reduced tillage, structure lime, turbidity*

Introduction

Transport of pesticides via sub-surface drains can contribute significantly to contamination of surface waters and soil management has been suggested as an important approach to reduce this transport (Brown & van Benium, 2009). The widely used substance glyphosate [*N*-(phosphonomethyl)glycine] is known to react with metal ions and to be strongly sorbed to soil minerals. The substance has four pK_a values (0.8, 2.3, 6.0 and 11.0) whereas the acid of phosphorus (P) has only three (2.2, 7.2 and 12.4). Long persistence of glyphosate has been reported after application in autumn to clay soils in the boreal zone (see e.g. Laitinen et al., 2009; Bergström et al., 2011), together with frequent occurrence of macropore flow

(Verecken, 2005; Jarvis, 2007; Kjær et al., 2011). Despite this, few studies have examined leaching of particulate glyphosate (PGly) via tile drains (Borggaard & Gimsing, 2008). In contrast, leaching of particulate-bound P, which has similar binding and sorbing characteristics to glyphosate, is frequently reported to be high from clay soils (see e.g. Uusitalo et al., 2001). Several studies have stressed the importance of structure in clay soils for the magnitude of glyphosate losses and losses of other strongly adsorbed pesticides through drainage. In addition to changes in macropore connectivity, the sorption and degradation of glyphosate may be altered as a result of tillage. However, published results regarding glyphosate leaching from reduced tillage compared with conventional ploughing have been contradictory. Lysimeter studies have shown no differences or modest positive or negative differences under reduced tillage compared with conventional ploughing, (Formsgaard et al., 2003; Gjetterman et al., 2009; Larsbo et al., 2009). On the other hand, several field experiments have demonstrated distinct positive differences in glyphosate losses via surface runoff under reduced tillage compared with mouldboard ploughing (e.g. Stenrød et al., 2007).

Reduced tillage, here referred to as shallow tillage, means that the soil is only tilled to a depth of 5-15 cm with a cultivator, disc harrow or rotovator and the soil is not inverted. This leaves the soil surface covered with at least 15% of crop residues year-round, according to the US definition (ASAE, 2006). Studies of different tillage techniques and associated P losses have revealed that shallow tillage can result in less detrimental compaction in the long term, as a result of plough pan development being avoided (Wither et al., 2007). Improved water storage and a reduction in evaporative water losses may follow (Aura, 1999). Increased biological activity and improved soil structure due to an increased amount of organic matter in the surface layers are other possible benefits (Rasmussen, 1999). On the other hand, shallow tillage by cultivator in wet conditions may create more cloddy topsoil compared with conventional mouldboard ploughing (Børresen & Njøs, 1993). In addition, conventional ploughing can disrupt macropores and reduce hydraulic conductivity below tillage depth, consequently decreasing losses of glyphosate with drainage water.

A possible method to improve soil structure and reduce glyphosate leaching losses is structure liming**.** Quicklime (calcium oxide, CaO) was widely used in the past in Sweden to stabilise agricultural clay soils and improve soil structure (Berglund, 1977). An immediate improvement in soil stability and porosity and aggregate strength has been reported (Choquette et al., 1987), caused by the ‘Pozzolan reaction’ (Shi & Day, 1993). In addition, dispersed clay particles may form soil aggregates as a result of flocculation and agglomeration (Prusinski & Bhattacharja, 2005). The clay may also be stabilised as a result of ion exchange between positive ions on clay surfaces and Ca ions (Rodriguez-Navarro et al., 2005). Such ion exchange was suggested as the major reason for significantly reduced P concentrations in drainage water on mixing lime (shale ash) into trench backfill in a slightly acid clay loam in Lithuania (Šaulys & Bastienė, 2007).

The main objectives of the present study were to quantify and evaluate glyphosate leaching and identify some possible mitigation options, in parallel with measures to reduce P leaching. Field studies were carried out to test the following hypotheses: i) A significant proportion of glyphosate leaching losses occurs in particulate form; ii) structure liming reduces glyphosate leaching losses compared with unlimed soils that are either conventionally ploughed or shallow-tilled; and iii) structure liming increases soil aggregate stability compared with unlimed soils that are either conventionally ploughed or shallow-tilled.

Materials and methods

Experimental plots and soil

In 2006, an experimental field with a subsurface drainage water collection system was constructed close to the Lake Bornsjön reservoir by Stockholm Water Company. It encompasses 28 drained plots, 20 of which were used in the present experiment. In order to match the experimental plots to farm machinery, their dimensions are 20 m x 24 m (0.048 ha) and the drains are placed centrally, with 8 m spacing, in order to effectively drain the soil. Drainage water flows to a sampling and measuring station and is recorded with tilting vessels and data logger. The data logger controls the flow-proportion sampling by means of small tube pumps in the basement of the station. After a certain volume of water has passed, the suction tube is first cleaned by reverse pumping and thereafter a small volume is sampled. The flow-proportional (composite) sampling took place in dark glass vessels (2.5 L) at relatively cold temperature (approximately 10-14^{o}C) and in darkness for a maximum of one week prior to freezing the water samples and transport to the laboratory before analysis.

Clay content (60%), is high throughout the profile (Table 1), with small spatial variation in both topsoil and subsoil (variance less than 0.5%). In addition, pH and soil concentration of P are uniformly distributed in the experimental area (variance less than 15%). In the soil profile, the pH (dry soil samples) varies between 5.2 and 6.9, with the lowest values occurring in the

70-100 cm layer, which includes the tile drains at approx. 90 cm depth. Under wet conditions the pH in the upper subsoil is higher than that under dry conditions (6.9 compared with 6.6). No carbonates have been detected. Plant-available P, analysed after extraction with acid ammonium-lactate solution (PAL) or as POlsen, is low, especially in the upper subsoil. The content of iron (Fe), analysed as lactate-extracted Fe (Fe AL) or as oxalate-extracted Fe (Feox), is high, while the corresponding aluminium values (AlAL and Alox) are rather typical for Swedish clay soils (Eriksson et al., 2012). Molar-based degree of P saturation in the lactate-extract (DPSAL) and the corresponding ratio between Olsen-P and P sorption, measured as sorption index (PSI2) are both low. Overall, the soil profile generally demonstrates a high ability to sorb P to the soil matrix.

The soil horizon has a strongly aggregated structure, with approximately 10 wide and 10-20 cm prismatic aggregates in the deeper part (43-100 cm). Large vertical pores (up to 5 mm wide) are apparent between the aggregates and abundant fine pores in old root channels. Frequent precipitation of rust occurs in the root channels, on aggregate walls and as 3 mm diameter patches and water retention is very high. This rust covers 10% of the area in the deeper horizon. In an adjoining field with an old drainage system, the deeper soil horizon is very wet, the aggregates similarly very prismatic and the structure is easily destroyed by digging.

Glyphosate application and cultivation practices

In preceding years the crops were: winter wheat in 2007, spring barley in 2008 and 2009 and oats in 2010. No glyphosate had been applied to the actual experimental plots for the previous 3 years. Quicklime (CaO) had been applied in dry conditions on the stubble in four plots in 2007 at a rate of 5 ton ha^{-1} and incorporated immediately into the soil by a cultivator driven in different directions. Since this initial year, the structure-limed plots have been conventionally ploughed in autumn.

Glyphosate was applied on 22 September 2010 as the commercial product Glypro Bio, at a rate equal to 1.06 kg ha^{-1} active substance. This amount, which represents a normal dose in Swedish production systems, was applied in evening at air temperature 11^{o}C and no wind. Twelve days later, the conventional and structure-limed plots were stubble-harrowed (Table 2) and 8 plots were shallow-tilled (12 cm) twice and reconsolidated with a rib-roller. After a further 10 days, the conventionally ploughed plots (8) and the structure-limed plots (4) were mouldboard-ploughed and the soil was inverted to a depth of 23 cm. All tillage operations took place under relatively dry soil conditions and without any pronounced cloddiness in the reconsolidated topsoil after cultivation.

Weather, discharge and water taken to analysis

Autumn 2010 was short, with permanent snow from the end of November (Figure 1). Owing to the thickness of the snow cover, soil freezing was limited despite low air temperatures. A short period of snowmelt occurred at the beginning of January, but this was followed by more accumulated snow. The main snowmelt took place in late March and the first two weeks in April.

The glass vessels with flow-proportional samples in the station basement were observed regularly (at least weekly) and when at least 300 mL turbid water had been collected from most plots, subsamples were taken from every plot for glyphosate analysis. The glass vessel was shaken and a portion of water was poured into a 200 mL plastic bottle. This was frozen at -18^{o}C before analysis for glyphosate and turbidity, which took place 5-8 months after sampling. Simultaneously, from every plot a 100 mL sample was taken in a glass bottle for P analysis and a 100 mL sample in a plastic bottle for pH analysis. These were immediately sent to the water laboratory where pH was measured on the following day, dissolved reactive P (DRP) within two days and total P (TotP) within 4 days after storage at +4^{o}C. When a minor amount of flow-proportional water was collected this was thrown away and the glass vessel was rinsed with distilled water. When there was a moderate amount of water or less turbid water in the glass vessel, sampling was performed only for analysis of P and turbidity for reasons of economy. Such sampling occurred in total on 5 sampling occasions. On March 28, 186 days after glyphosate application in autumn, turbidity was observed once again in the flow-proportionally sampled water and additional water was collected for glyphosate analysis, which was performed on the 14 most turbid samples.

Water analysis

Total P was analysed as soluble molybdate-reactive P after acid oxidation with $K_2S_2O_8$ (ECS 1996). Dissolved reactive phosphorus (DRP) was analysed after pre-filtration using filters with pore diameter 0.45 µm (Schleicher & Schüll GmbH, Dassel, Germany). In the major flow events and with water-saturated topsoil the concentration of dispersed clay is known to be high at the present site (Ulén & Persson, 1999). Particulate P (PP) is the absolute dominant P fraction, while non-mineral forms of dissolved P are very small, and accordingly the difference between TotP and DRP was taken as PP. The concentration of particles was analysed from thawed samples as turbidity on a HACH 2100 turbidometer (Hach Loveland, Co, Düsseldorf, Germany). Measurement took place 15 sec after shaking the sample and the results were expressed as nephelometric turbidity units (NTUs). Freezing-thawing and shaking may have broken down any larger aggregates in particulate form into smaller particles, reducing shadowing and facilitating turbidity measurement.

Before analysing glyphosate, each thawed sample was thoroughly shaken by hand and 20 g were immediately transferred to a polypropylene centrifuge filter tube containing a removable cellulose acetate filter with pore size 0.45 µm (#64525-CA, SUN-SRi, Tennessee, USA). The tube was centrifuged at 4000 rpm for 2 minutes. The filtered water was used for analysis of DGly, including AMPA, after pH adjustment (pH 7-8) with either diluted HCl or NaOH.

The removable filter in the tube, containing the particles (PGly), was immediately transferred to a new, filter-free, centrifuge tube. An internal standard mixture (0.1 µg L^{-1}) of glyphosate isotope-$^{13}C^{15}N$ and 0.2 µg L^{-1} of the same isotope of its major metabolite aminomethyl-phosphonic acid (AMPA) was added. Extraction was performed using 5 mL 0.1 M NaOH, with occasional shaking of the sample for 15 min. The sample was then centrifuged for 1-2 min at 3000 rpm. Another 3 mL 0.1 M NaOH were used for rinsing and the sample was shaken and immediately centrifuged at 3000 rpm. The filter was removed and sample pH was adjusted to pH 2 by adding 0.6 M HCl, during an hour, in order to precipitate any humic acids. The sample was then diluted and neutralised (pH 7-8) with 0.1 M NaOH.

The same analytical procedure was used for both PGly and DGly and involved ion-exchange and derivatisation, followed by final identification and quantification by gas chromatography-mass spectrometry (GC-MS). The internal glyphosate/AMPA standard mixture was added (also to the DGly samples) before starting analysis. Sample preparation involved series coupling of an empty reservoir, an activated C18-column (Isolute 500g, Biotage IST, Uppsala Sweden) and a wet bead ion-exchange resin (AG 1-X8, Bio-Rad Laboratories, Sundbyberg, Sweden). The whole sample was entered into the reservoir and the water moved slowly through the cleaning and ion-exchange stages. The ion-exchange column was thereafter slowly eluted with 10 mL 0.6 M HCl into a 25 mL pear-shaped bottle (pre-washed with KOH). The extract was evaporated to almost dryness using vacuum and a 50 °C water bath, and then the remaining liquid was transferred into a glass tube (prewashed with

KOH). The pear-shaped bottle was rinsed with methanol/ultrapure water/HCl (80/20/1.4) and this too was transferred to the glass tube. The sample was thereafter blown to total dryness by air at 50 °C.

Derivatisation was performed using 1.5 mL trifluoroacetic anhydride (TFAA) and 0.75 mL trifluoroethanol (TFE), followed by heating to 100 °C during 1 hour. After being cooled to room temperature the sample was evaporated to total dryness for at least 2 hours by air. The sample was thereafter dissolved in 0.5 mL ethyl acetate (EtAc).

Analyses were performed using gas chromatography-mass spectrometry (GC-MS) with a Hewlett-Packard 6890 GS MS 5973 (Agilent Technology AB, Kista, Sweden), equipped with a capillary column (HP-5MS Ul), a split/splitless injector and the software Chemstation. A 1 µL portion of the sample was injected in pulsed splitless mode at oven temperature 70 °C. After 1 min, the oven temperature was raised to 160 °C at a rate of 16 °C min^{-1} and then from 160 to 260 °C at a rate of 70 °C min^{-1}. Helium (N55) was used as the carrier gas and the flow rate was 1.2 mL min^{-1}. The mass spectrometer was operated in the electron impact (EI) mode; the transfer line temperature was 260 °C and the MS source temperature 230 °C. Fragment ions were detected by selected ion monitoring (SIM) and used for identification of AMPA and glyphosate derivates. Verification of compound identification was based on comparison of the peak-heights of the selected ions in the samples with those of the standards. The uncertainty of residue results was estimated from the recoveries obtained. The limit of detection (LOD) was 0.03 µg L^{-1}, 0.1 µg L^{-1} and 0.2 µg L^{-1} for DGly, PGly and AMPA respectively, with occasional higher LODs due to background interference. The limit of quantification (LOQ) was 2-3 times higher.

Soil aggregate stability

Soil samples from plots with structure liming, conventional ploughing and reduced tillage were analysed in the laboratory for aggregate stability, expressed as readily dispersed clay (RDC). Slightly moist samples were collected from the topsoil (0-20 cm) on 27 August 2010, before post-harvest stubble cultivation, and gently transported to the laboratory. Four subsamples representing 12 aggregates (8-10 mm) were prepared for each plot and gently wet-sieved (0.6 mm mesh opening) with a slow oscillating movement (90 revolutions min^{-1}) in 3 cm vertical sweeps for 6 min (Ejkelkamp Wetsieving Equipment, Gesbieek, The Netherlands). After 4 hours sedimentation (to allow all particles larger than clay to settle;

Sheldrick & Wang, 1933), the content of dispersed clay still in solution was determined by turbidometer (Cryz et al., 2002).

Data calculations and statistical analyses

The mean and standard deviation were calculated for the experimental parameters determined in all flow-proportional samples (4 or 8 parallel samples) from replicate plots for the different treatments. If no residue of glyphosate or AMPA was detected in a given sample, the value 0 was used for calculating the mean. Pearson correlation and regression linear relationships were determined between the parameters total glyphosate (TotGly = PGly + DGly), TotP, PGly, PP and turbidity for the autumn period (27 September-15 November) and between TotP and turbidity for the spring period (21 March-11 April). Any differences in glyphosate concentrations between the different soil treatments were analysed using Bonferroni post test assuming equal variance and a significance level of $p<0.05$.

Leaching losses from the different plots in the autumn period were calculated by multiplying discharge by measured flow-proportional concentrations in the sub-periods. In the spring period, transport of TotGly was estimated from measured values from 14 plots on 28 March. Without any measured values the transport was estimated from TotP transport using the relationship between TotP and TotGly as determined for the 14 samples.

Results and discussion

Glyphosate and phosphorus concentrations in water

One week after glyphosate application in autumn, when 10 mm discharge had passed through the tile drainage system, no glyphosate or AMPA was present in detectable quantities in the discharge (Table 3). In the following 7-8 weeks, representing 70 mm water discharge, relatively high and quantifiable concentrations of both DGly and PGly were detected in practically all water samples and, in addition, dissolved AMPA was frequently observed. The concentrations varied greatly from plot to plot and TotGly concentrations of up to 5-6 µg L^{-1} were recorded for some plots. High PGly concentrations were generally associated with high DGly concentrations and the two forms of glyphosate were significantly correlated to each other ($p<0.05$). More DGly seemed therefore to leach together with mobilised soil particles with high glyphosate content. However, since glyphosate sorption-desorption reactions are rapid (see e.g. Borggaard & Gimsing, 2008), the correlation may also reflect an equilibrium taking place between PGly and DGly in the cumulative discharge stored before filtration.

Mean DGly concentration in discharge in the autumn was 1.03 µg L^{-1} for plots with shallow tillage; 0.43 µg L^{-1} for plots with conventional ploughing and 0.36 µg L^{-1} for plots with structure liming (differences not significant).

Similarly to TotGly, the majority of TotP appeared in particulate form. A clear and positive correlation between TotGly and TotP concentrations and between PGly and PP concentrations was recorded (Figure 2). In turn, PP concentrations could be quite well predicted from turbidity (Figure 2). In contrast, DRP concentrations were generally low (0.018-0.027 mg L^{-1}) and DGly concentrations were more weakly correlated to DRP concentrations ($r=0.65$; $p<0.001$). Glyphosate is commonly suggested to compete with phosphate ions for adsorption sites (Borggaard & Gimsing, 2008), but at the present site, with high sorption capacity of the soil particles, this seemed not to be the case, since the correlation was positive. Mean PGly concentrations in the autumn were 1.73 µg L^{-1} in discharge from shallow tilled plots; 0.62 µg L^{-1} for conventional ploughed plots; and 0.36 µg L^{-1} for structure-limed plots, which were all significantly different ($p=0.001$).

Glyphosate and phosphorus in spring versus autumn period

As with glyphosate and phosphorus, pH was measured in the cumulative flow-proportionally sampled water and may have changed in the glass vessel. However, measured pH generally did not differ between the three treatments and pH in discharge from the previously structure-limed plots was similar to that in discharge from the unlimed plots (Table 3). The pH tended to be lower (6.6) in the snowmelt period (Table 3). This low pH may have influenced both the electrical charge of glyphosate and the hydrogen bonds of the minerals (Verecken, 2005), which may explain the high concentrations of DGly in snowmelt. The snowmelt water had low electric conductivity and DRP concentrations that were twice as high as those in the autumn discharge water. High DRP concentrations in snowmelt are frequently observed for high charged Swedish clay soils, which commonly contain the mineral illite (Ulén, 2003; Ulén & Snäll, 2007). In addition, the relatively low pH may dissolve some Ca-bound P from the clay particles (Devau et al., 2011). The PGly concentrations found in snowmelt in the present study were generally lower than the DGly concentrations and remained at nearly the same level as in autumn, and consequently the relative proportions of DGly and PGly were reversed from autumn to spring (snowmelt) (Table 4). However, the latter case is based on a more limited number of analyses (n = 14). The PGly/turbidity ratio was generally 20-40% lower in March than in November and the dispersed clay particles might have been more decomposed and depleted of glyphosate in spring. Similarly, PP concentrations related to turbidity had a lower slope in snowmelt than in autumn. The regression line (not shown) was: [PP] (μg L^{-1}) = 11 + 0.7818* Turbidity (FTU) (R^2 = 92%). This may also have been an effect of the topsoil colloids being more depleted of P in spring than in autumn.

Since the major water discharge took place during the snowmelt period, glyphosate losses tended to be higher in spring than in autumn (Tables 5 and 6). In relation to applied amount, losses were approximately 0.1% in spring and 0.05% in autumn for the conventionally ploughed plots. The main reason for the high spring discharge was the intensive snowmelt taking place after a winter with much snow accumulation. The apparent importance of such a snowmelt period for glyphosate losses confirms findings by Laitinen et al. (2009). Snow accumulation also had great consequences for P losses, e.g. for the conventionally ploughed plots TotP leaching losses were 0.32 kg ha^{-1} in the snowmelt period, compared with 0.12 kg ha^{-1} in autumn.

Glyphosate and phosphorus losses under different soil management regimes

In the autumn period, TotGly leaching losses were on average 0.70 g ha^{-1} from the conventionally ploughed plots (Table 6). TotGly losses from structure-limed plots were significantly lower ($p<0.05$) than from shallow-tilled plots, expressed in absolute terms (Table 5), and also as a percentage of applied amount of glyphosate (Table 6). The structure-limed plots had significantly ($p<0.05$) better aggregate stability (lower RDC values) in autumn than the conventionally ploughed and shallow-tilled plots (Figure 3), which may explain the clear tendency for lower losses of both PGly and PP from this treatment (Table 5).

Any enhanced amounts of stubble residues in the topsoil, combined with higher potential biological activity and organic matter content, did not seem to have improved aggregate stability in the regular shallow-tilled plots (Figure 3). Furthermore, leaching losses of both PGly and PP tended to be highest from these plots (Table 5). Sorption of glyphosate is generally not increased in the presence of more straw residues as a consequence of reduced tillage (Stenrød et al., 2007), so the straw may have facilitated water transport rather than providing new sorption sites after the mixing and reconsolidation of the soil surface. Since the tillage operations took place under relatively dry soil conditions, no serious soil compaction with associated soil structural problems should have occurred. However, the macropores might have been less damaged after shallow tillage, allowing more channelised water flow through the soil profile. Shallow tillage is possibly a suitable mitigation option primarily for sloping sites with surface erosion and a high risk of particle-facilitated leaching of glyphosate. This is also the case as regards leaching of P at the experimental site with no slope and, similarly, P losses were reported to be higher with reduced tillage than conventional tillage at a Finnish site (Koskiaho et al., 2002).

Since there were strong similarities between phosphorus and glyphosate concentration pattern, TotGly could act as an indicator of leaching losses of P, including PP. The source of the glyphosate leaching in this study was the tilled topsoil (0-12 or 0-23 cm), which was possibly the main source of phosphorus leaching too. Other studies have also reported that the topsoil may act as the main source of particle and PP losses via subsurface runoff (see e.g. Chapman et al., 2001).

Conclusions

In this field study, glyphosate leaching followed the same general pattern as phosphorus leaching. A significant proportion of glyphosate leaching losses may occur in particulate form from clay soils with high amounts of sorption sites available. The fine clay particles may act as an important transporter of glyphosate via tile drains. Structure liming combined with conventional ploughing was shown to reduce glyphosate leaching losses compared with unlimed soils at the study site, while simultaneously improving soil aggregate stability significantly. The results also showed that shallow tillage may not be a suitable way to reduce particle-facilitated transport of glyphosate and phosphorus via tile drains from this type of clay soil.

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Table 1. Selected physical and chemical properties of the soil at the study site

Properties	Soil depth (cm)					Reference for the Method
	0-10	10-30	30-50	50-70	70-100	
Particle size distribution:						
<0.002 mm (clay) (%)	60	60	59	61	54	Eriksson et al., 1998
0.002-0.02 mm (%)	31	30	30	31	34	Eriksson et al., 1998
0.02-0.2 mm (%)	9	10	11	8	12	Eriksson et al., 1998
Organic matter (%)	3.9	1.9	0.1	0.0	0.0	Eriksson et al., 1998
$pH_{H2O}{}^{*}$	6.0	6.2	6.6	6.5	5.2	ISO, 2005
P_{Olsen} (mmol kg^{-1})*	0.59	0.53	0.13	0.17	0.68	Olsen & Sommers, 1982
P_{AL} (mmol kg^{-1})*	1.4	1.0	0.3	0.4	1.0	Egnér et al., 1960
Al_{ox} (mmol kg^{-1})*	116	106	71	77	88	Schwertmann, 1964
Fe_{ox} (mmol kg^{-1})*	165	169	158	181	118	Schwertmann, 1964
Al_{AL} (mmol kg^{-1})*	10.3	9.9	9.8	9.6	16.1	Ulén, 2006
Fe_{AL} (mmol kg^{-1})*	9.4	10.1	8.8	9.4	12.5	Ulén, 2006
PSI_2 (mmol kg^{-1}) *	7.3	7.8	7.3	7.2	10.5	Börling et al., 2004
$P_{Olsen}/PSI_2{}^{*}$ (%)	8.1	6.8	1.8	2.4	6.4	Börling et al., 2004
$DPS_{AL}{}^{*}$ (%)	8.7	6.2	2.0	2.5	4.3	Ulén, 2006

*data from Andersson et al., 2012

Table 2. Management regime in the different treatments (A-E) in 2010, where A+B (8 plots) represent regular conventional autumn ploughing, C (4 plots) represents previous structure liming and D+E (8 plots) represent regular shallow tillage in autumn

Treatment	Management	Date
A+B, C, D+E	Harrowing (0-5 cm)	16 May
A+B, C, D	Fertilisation, seed drilling*	17 May
E	Fertilisation (broadcasting)	17 May
A+B, C, D+E	Sowing (oats)	17 May
A+B, C, D+E	Harvesting	27 Aug.
A+B, C, D+E	Glyphosate application (1.06 kg ha^{-1})	22 Sept.
A+B, C	Stubble harrowing	4 Oct.
D+E	Cultivation (8 cm) twice	4 Oct.
A, B, C	Conventional ploughing (23 cm)	14 Oct.

* No P fertilisation to B plots

Table 3. Discharge, pH (in stored composite samples) and flow-proportional concentrations of dissolved glyphosate (DGly), AMPA, particulate glyphosate (PGly), dissolved reactive phosphorus (DRP), particulate P (PP) and turbidity (Turb) in five periods 2010-2011 (n.d. = not detected)

Period	22/9-27/9	28/9-25/10	26/10-8/11	8/11-15/11	21/3-28/3
Conventional ploughing					
Discharge (mm)	8.2±3.0	9.2±4.3	25.5±11.1	33.5±13.1	72.9±30.2
pH	6.5	7.2	7.0	6.7	6.6
DGly (μg L^{-1})	n.d.	0.43±0.32	0.43±0.34	0.39±0.21	0.31±0.34
AMPA (μg L^{-1})	n.d.	0.05	0.04	0.03	n.d.
PGly (μg L^{-1})	n.d.	0.67±0.63	0.61±0.67	0.60±0.34	0.22±0.43
DRP (mg L^{-1})	0.021±0.011	0.021±0.011	0.018±0.007	0.020±0.007	0.048±0.019
PP (mg L^{-1})	0.132±0.068	0.122±0.010	0.161±0.166	0.168±0.144	0.124±0.039
Turb (NTU)	64±26	36±7	62±24	60±20	30±16
Structure liming					
Discharge (mm)	10.4±4.1	13.5±5.4	29.1±11.4	30.1±5.1	74.4±25.5
pH	6.9	7.3	7.2	6.9	6.6
DGly (μg L^{-1})	n.d.	0.24±0.20	0.30±0.21	0.24±0.27	0.23±0.25
AMPA (μg L^{-1})	n.d.	0.03	e.d.	0.05	0.08
PGly (μg L^{-1})	n.d.	0.40±0.48	0.41±0.53	0.33±0.58	0.16±0.35
DRP (mg L^{-1})	0.018±0.007	0.017±0.008	0.015±0.005	0.020±0.006	0.047±0.027
PP (mg L^{-1})	0.075±0.066	0.066±0.074	0.093±0.131	0.100±0.106	0.078±0.032
Turb (NTU)	46±30	34±11	64±26	46±31	28±6
Shallow tillage					
Discharge (mm)	10.8±5.3	15.6±6.6	25.9±10.2	29.7±6.4	76.4±23.5
pH	6.8	7.2	7.1	6.8	6.6
DGly (μg L^{-1})	n.d.	1.15±0.89	1.28±1.42	0.99±0.64	0.82±0.93
AMPA (μg L^{-1})	n.d.	0.05	0.23	1.3	0.02
PGly (μg L^{-1})	n.d.	1.99±1.64	1.42±1.44	1.89±1.48	0.57±0.84
DRP (mg L^{-1})	0.024±0.007	0.024±0.007	0.023±0.008	0.027±0.007	0.047±0.021
PP (mg L^{-1})	0.142±0.078	0.236±0.181	0.411±0.355	0.275±0.151	0.136±0.029
Turb (NTU)	88±44	50±17	99±45	81±31	52±43

Table 4. Number of samples analysed (n), relative proportions of dissolved glyphosate (DGly) and particulate glyphosate (PGly) in total glyphosate (TotGly) and relative proportions of dissolved reactive P (DRP) and particulate P (PP) in total phosphorus (TotP) in autumn (28/9-15/11 2010) and in a snowmelt period in spring (21-28/3 2011), based on flow-proportional concentrations

Glyphosate			Phosphorus		
Fraction	Autumn	Spring	Fraction	Autumn	Spring
n	80	14	No	80	20
DGly/TotGly (%)	40	60	DRP/TotP (%)	10	32
PGly/ TotGly (%)	60	40	PP/TotP (%)	90	68

Table 5. Discharge and transport of dissolved glyphosate (DGly), particulate glyphosate (PGly), total glyphosate (TotGly), dissolved reactive phosphorus (DRP), particulate P (PP) and total P (TotP) from conventionally ploughed, structure-limed (and ploughed) and shallow-tilled plots in the period 28/9-15/11 2010

Period 28/9-15/11	Conventional	Structure-limed	Shallow-tilled
Discharge (mm)	69±28	74±23	72±22
DGly (g ha^{-1})	0.25±0.13	0.12±0.10	0.65±0.54
PGly (g ha^{-1})	0.45±0.53	0.19±0.19	1.01±0.75
TotGly (g ha^{-1})	0.70±0.60	0.31±0.31**	1.65±0.96
DRP (kg ha^{-1})	0.012±0.004	0.012±0.003	0.018±0.007
PP (kg ha^{-1})	0.104±0.082	0.048±0.044	0.192±0.111
TotP (kg ha^{-1})	0.117±0.084	0.060±0.044	0.209±0.114

** Significantly lower ($p<0.05$) than in shallow-tilled plots

Table 6. Discharge (mm) and leaching losses of dissolved glyphosate (DGly), particulate glyphosate (PGly) and total glyphosate (TotGly) as a percentage of original amount applied from conventionally ploughed, structure-limed (and ploughed) and shallow-tilled plots based on measurements in autumn (28/9-15/11 2010) and more rough estimates in the most intensive spring snowmelt period (31/3-11/4)

	Conventional		Structure-limed		Shallow-tilled	
	Autumn	Snowmelt	Autumn	Snowmelt	Autumn	Snowmelt
Discharge (mm)	69	170	74	169	72	160
DGly (%)	0.024	-	0.011	-	0.061	-
PGly (%)	0.041	-	0.018	-	0.095	-
TotGly (%)	0.066	0.09	0.029	0.05	0.156	0.19

FIGURE CAPTIONS

Figure 1. Temperature
(^{o}C), precipitation (mm) and snow cover (mm) on the experimental field in 2010-2011.

Figure 2. Regression equation for the relationship between concentrations of: a) total glyphosate (TotGly) and total phosphorus (TotP); b) particulate glyphosate (PGly) and particulate P (PP); and c) PP and turbidity (NTUs) in the period 27 September-15 November 2010. Corresponding Pearson correlations (0.86, 0.84 and 0.82, respectively) were all significant ($p<0.001$).

Figure 3. Readily dispersed clay (RDC) in the topsoil from (A) conventionally ploughed, (C) structure-limed and (D) shallow-tilled plots. The soil was sampled in September 2010, three years after structure liming.

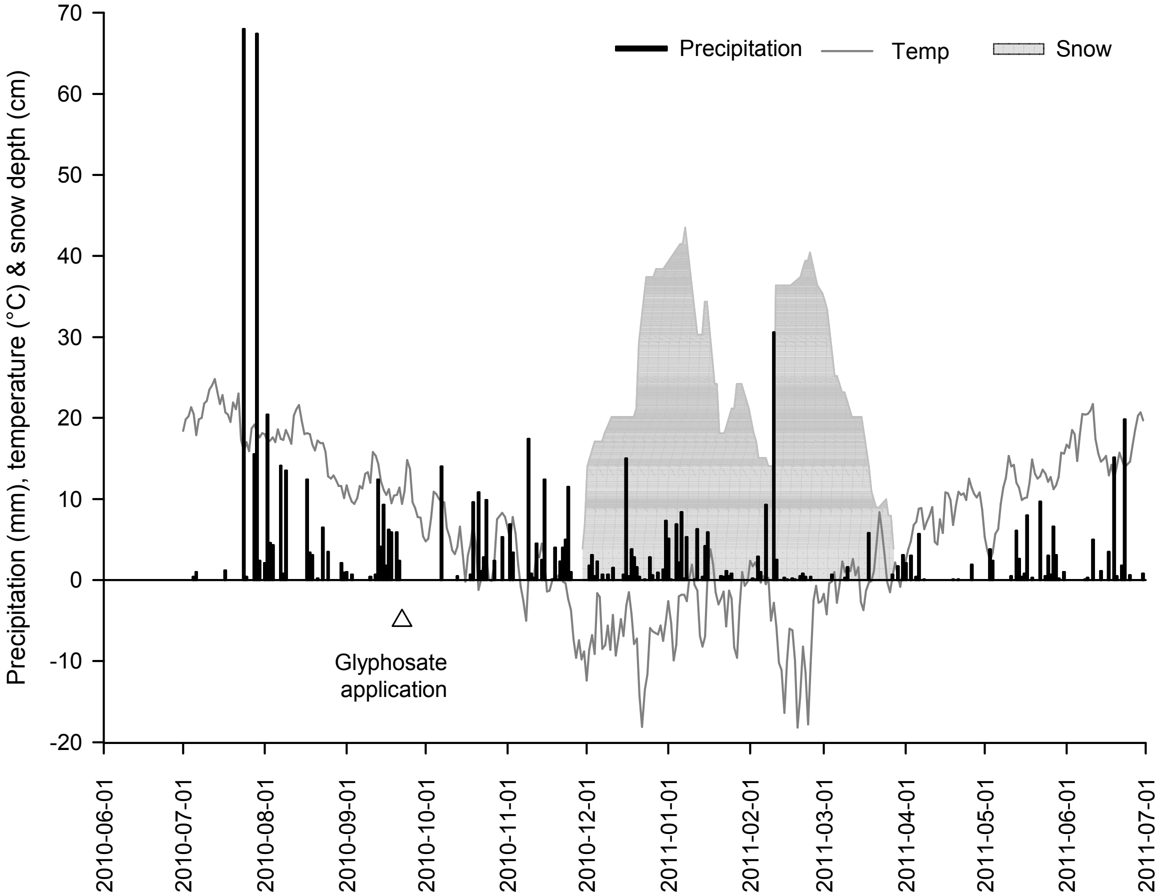
Precipitation
Temp
Snow
Precipitation (mm), temperature (°C) & snow depth (cm)
70
60
50
40
30
20
10
0
-10
-20
△
Glyphosate application
2010-06-01
2010-07-01
2010-08-01
2010-09-01
2010-10-01
2010-11-01
2010-12-01
2011-01-01
2011-02-01
2011-03-01
2011-04-01
2011-05-01
2011-06-01
2011-07-01

Fig 1

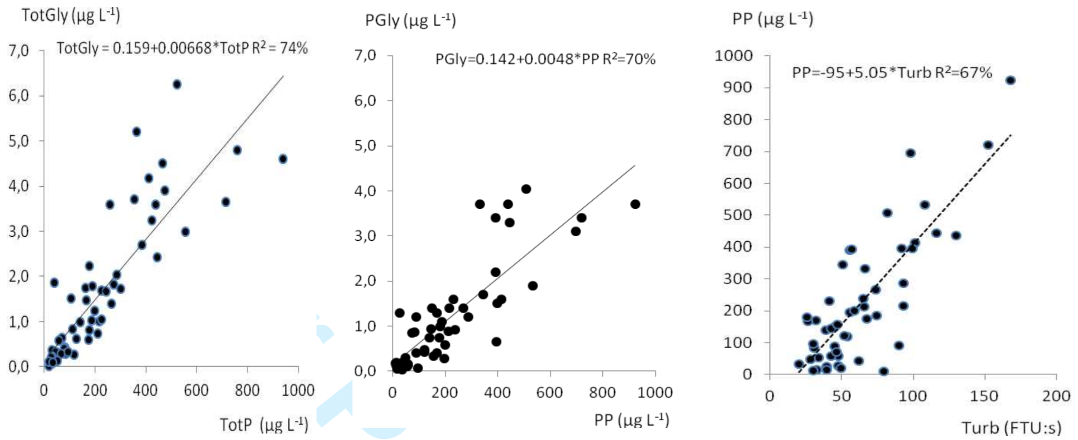
TotGly (µg L-1)
TotGly = 0.159+0.00668*TotP R2 = 74%
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
200
400
600
800
1000
TotP (µg L-1)
PGly (µg L-1)
PGly=0.142+0.0048*PP R2=70%
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
200
400
600
800
1000
PP (µg L-1)
PP (µg L-1)
PP=-95+5.05*Turb R2=67%
1000
900
800
700
600
500
400
300
200
100
0
0
50
100
150
200
Turb (FTU:s)

Fig 2

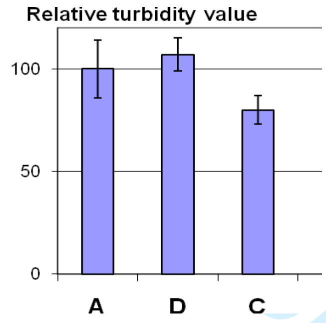

Fig. 3