Surface and subsurface transport pathways of pesticides to surface waters

Improving understanding of the effects of spatial and temporal variation in soil properties

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Cover: The stream draining a small Swedish agricultural catchment where the monitoring of pesticide concentrations presented in this thesis was conducted.
(photo: M. Sandin)

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Abstract

Risk assessment and mitigation of pesticides losses to surface waters is a major challenge due to spatial and temporal variation in the factors that influence underlying transport processes. This thesis examines effects of spatial and temporal variation in soil properties on such losses and the pathways along which the transport occurs. Spatial variation in pesticide concentrations in streamflow were monitored in a small Swedish agricultural catchment with a large variation in soil types. Temporal variability in the structural and hydraulic properties that largely control the partitioning between surface and subsurface runoff was examined through field measurements and laboratory experiments.

Considerable changes in the volume, size distribution and connectivity of structural pores due to rainfall were observed in the harrowed layer after tillage, both in the field and the laboratory. In the field these changes were associated with decreases in near-saturated hydraulic conductivities of around one order of magnitude. Effects of wetting and drying on total porosity and the pore size distribution (PSD) varied between soils of different texture and organic carbon content. Post-tillage changes in soil structural and hydraulic properties could be accounted for in mechanistic models as changes in total porosity and the PSD and functions relating soil properties to the magnitude of these changes should be useful for parameterization. The ability to predict pesticide losses through surface runoff could thus be expected to increase.

At the catchment scale, consistently larger numbers of compounds at larger concentrations were found in a sub-catchment with a relatively large proportion of clay soils than in a sub-catchment with a smaller proportion of such soils. Only a few compounds at trace concentration were found in a third sub-catchment with coarser- textured soils. Temporal stability of this spatial pattern suggests that the relative risk of pesticide losses to surface waters is related to soil properties under Swedish agro-environmental conditions. Soil texture maps could thus be used as a simple method for identification of high-risk areas. In the studied catchment, which is to a large extent subsurface drained and where surface connectivity between fields and the stream is limited, drainage was found to be a more likely dominant transport pathway than surface runoff.

Keywords: pesticide losses, surface waters, transport pathways, soil properties, spatial and temporal variation

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Dedication

Oh yes!

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Sandin, M., Koestel, J., Jarvis, N., Larsbo, M. (2017). Post-tillage evolution of structural pore space and saturated and near-saturated hydraulic conductivity in a clay loam soil. *Soil & Tillage Research*, 165, pp. 161-168.

II Sandin, M., Jarvis, N., Larsbo, M. Consolidation and surface sealing of nine harrowed Swedish soils (manuscript)

III Sandin, M., Piikki, K., Jarvis, N., Larsbo, M., Bishop, K., Kreuger, J. (2017). Spatial and temporal patterns of pesticide concentrations in the stream of a small Swedish agricultural catchment (in revision, submitted to *Science of the Total Environment*)

Paper I is reproduced with the permission of the publishers.

The contribution of Maria Sandin to the papers included in this thesis was as follows:

I Planned the image and data analyses together with the co-authors. Performed the analyses and writing with assistance from the co-authors.

II Planned the image and data analyses together with the co-authors. Performed the analyses and most of the writing with assistance from the co-authors.

III Planned the study together with N. Jarvis, K. Bishop and J. Kreuger. Organized and carried out all the field work and performed the data analyses and writing with assistance from all co-authors.

Abbreviations

DT50	Degradation half-life of compound
GUS	Groundwater Ubiquity Score, index reflecting leaching potential of pesticide compounds (Gustafson, 1989)
K_{oc}	Soil organic carbon partitioning coefficient
K_{foc}	Freundlich organic carbon partitioning coefficient
K_s	Saturated hydraulic conductivity
PPDB	Pesticide Properties DataBase (Lewis et al., 2016)
PSD	Pore size distribution
SOC	Soil organic carbon

1 Introduction

Pesticides are used in modern agriculture to alleviate problems caused by weeds, insects and plant pathogens and have contributed to increasing both yields and food security. However, unintended and undesirable effects on non-target organisms may occur. Although it usually only constitutes a very small fraction of the applied amounts, pesticides can be transported from the site of application in agricultural fields to other environmental compartments (Burgoa and Wauchope, 1995; Capel et al., 2001; Brown and van Beinum, 2009). Monitoring has revealed that pesticide residues frequently occur in surface waters (Lindström et al., 2015), and numerous studies have reported concentrations where effects on aquatic organisms or communities can be expected (e.g. Schafer et al., 2011; Ali et al., 2014; Stone et al., 2014; Knauer, 2016; Houbraken et al., 2017).

The principal pathways along which this transport occurs are known. They include spray drift and atmospheric deposition, surface runoff, drainage and saturated subsurface flow, in addition to point source contamination (Holvoet et al., 2007; Reichenberger et al., 2007). Some previous research has shown that large diffuse losses of pesticides may be associated with locations in the landscape where the soil surface frequently becomes saturated, since this increases the risk of triggering rapid flow processes like surface runoff and macropore flow to drains (Leu et al., 2004b; Freitas et al., 2008) For example, Freitas et al. (2008) measured pesticide concentrations in surface water following controlled applications of different herbicides to a number of fields, as well as on the wettest part of one field (constituting 1% of the field area), in two small catchments in Switzerland. This study clearly demonstrated the effects of soil hydrology on pesticide losses to surface water. Losses of the compound applied to the wet patch were 24% of the applied amount as compared with 0.06 to 1.08% for the herbicides applied to the other fields. Losses were also much larger from fields in one of the catchments, which had a larger proportion of soils susceptible to surface runoff due to shallow groundwater.

The finding that soils with similar texture and structure often have a similar hydrologic response to rainfall has stimulated the development of classification schemes where the properties of soils and profiles or certain influential horizons are used to predict the expected runoff response (Boorman et al., 1995; Scherrer and Naef, 2003; Schmocker-Fackel et al., 2007; Schneider et al., 2007). The potential usefulness of such concepts for locating the main areas contributing to pesticide contamination of surface waters was demonstrated by Blanchard and Lerch (2000) in a study at the regional scale in the USA. They found that stream pesticide concentrations were correlated with broad runoff classes derived from soil maps. However, the significance and relative importance of soil properties for pesticide losses through fast surface and subsurface transport pathways has not been investigated under Swedish agro-environmental conditions. The limited understanding of the spatial and temporal distributions of the factors controlling pesticide losses to surface waters in Sweden makes both risk assessment and implementation of mitigation measures at farm, catchment and regional scales a tremendous challenge. Currently, as a result of this uncertainty, many mitigation measures are implemented in an over-conservative way. For example, grassed buffer strips installed along waterways to prevent surface runoff and erosion remove large areas of agricultural land from production, but may only be effective at a few localities where runoff is both generated and reaches the stream. There is therefore a great need for a better understanding of the main drivers of spatial variations in pesticide transport to surface waters as well as the temporal stability of such patterns. More effective ways of identifying locations and situations that could lead to unacceptable effects on surface water quality could both lead to more cost-effective implementation of mitigation strategies and more reliable risk assessments.

Models are widely used as decision-support tools in pesticide risk assessment and management. However, at present most such models rely on simplified empirical relationships, such as the USDA SCS curve number method, to predict the frequency and extent of surface runoff. More mechanistic modelling approaches could have some advantages, but their development is currently hampered by the difficulty of dealing with the temporal variability in soil structure and hydraulic properties that largely controls the partitioning of runoff between surface and subsurface pathways. An improved understanding of these processes is needed to support the development and parameterization of process-based models that could help identify areas vulnerable to surface runoff losses of pesticides, where buffer strips would be most effective.

2 Aims and objectives

The overall objective of the work presented in this thesis was to add to the current knowledge base on how spatial and temporal variation in soil properties affect losses of pesticides to surface waters. The specific aims of this thesis were:

- To quantify the post-tillage evolution of soil structural pore space and saturated and near-saturated hydraulic conductivity as well as the effect of soil properties such as particle size distribution and soil organic carbon content on the magnitude and direction of these changes (Papers I and II).
- To assess whether spatial variation in pesticide losses at the catchment scale can be related to variation in soil properties and to determine the relative importance of different surface and sub-surface transport pathways for such losses under Swedish agro-environmental conditions (Paper III).

In the following, I first give an overview of the current state of knowledge about pesticide occurrence in surface waters, the pathways along which the transport from agricultural fields to surface water occur, and the factors that influence their relative importance under different conditions. The three papers that support this thesis are then briefly summarized, followed by conclusions and a short discussion of future research needs and recommendations.

3 Pesticides in surface waters

Losses of pesticides to surface waters are of great concern as the occurrence of these xenobiotics in the aquatic environment may have harmful effects on individual species or entire ecosystems. They may also contribute to the contamination of drinking water resources. For example, Stone et al. (2014) concluded that one or more compounds were above chronic aquatic life benchmarks in 61% of monitored streams in agricultural catchments in the U.S. during 2002-2011. Lindström et al. (2015) summarized the results from the Swedish environmental monitoring program and found that 45% of all samples collected between 2002 and 2012 contained one or more compounds exceeding guideline values used to assess the environmental quality of surface waters. By compiling data from monitoring campaigns conducted in Swiss streams between 2005 and 2012, Knauer (2016) found that 16 of 60 considered compounds were detected at least once at concentrations above regulatory limits based on ecotoxicological studies.

Comprehensive assessment of the contamination status of surface water bodies and the associated risks of ecological effects is, however, a significant challenge. The very large number of potentially affected surface water bodies, as well as the large number of current and legacy compounds and generally limited funds forces researchers and public authorities in charge of environmental monitoring to prioritize their efforts. As a result, the occurrence of pesticides in the aquatic environment is generally only determined for a small proportion of relevant compounds (Moschet et al., 2014) and surface water bodies. A further complicating factor is that concentrations in streams can vary over several orders of magnitude over time, often with short-lived peaks that are easily missed with the infrequent sampling of many monitoring programs (Rabiet et al., 2010; Petersen et al., 2012; Stehle et al., 2013). Assessment of the risks associated with measured pesticide concentrations are also in many cases hampered by uncertain or limited ecotoxicological data (von der Ohe et al., 2011).

The large variation in sampling methods and frequencies as well as the types and numbers of compounds and water bodies makes comparison of results from different studies difficult. Some general conclusions regarding pesticide occurrence in surface waters may however be drawn. Pesticide concentrations are generally larger in small catchments with predominantly agricultural land use than they are in larger catchments (e.g. Kreuger and Brink, 1988; Schulz, 2004). Both within-stream processes such as transformation, sorption/sedimentation and volatilization (Capel et al., 2001) as well as dilution with water from non-agricultural areas can be expected to play a greater role at larger spatial scales. However, pesticides can still be the main toxic agents in large rivers (Schafer et al., 2011). Detection frequencies are highest during the main application season (Kreuger and Brink, 1988; Schafer et al., 2011) and generally the largest concentrations occur during rainfall-induced high-flow conditions (Neumann et al., 2002; Petersen et al., 2012). With the exception of some extreme events when more than 10% of the applied amount has been transported to surface waters, total losses are most often below 2% (Burgoa and Wauchope, 1995; Capel et al., 2001). Herbicides are generally more frequently detected and found in larger concentrations than fungicides and insecticides (Moschet et al., 2014; Stone et al., 2014; Lindström et al., 2015; Schreiner et al., 2016), largely reflecting differences in total usage and relative mobility in the environment. Several studies have found total losses to be strongly correlated with the applied amount (Burgoa and Wauchope, 1995; Kreuger and Tornqvist, 1998; Neumann et al., 2002). Another common finding, for pesticides as well as organic pollutants in general, is that only a few of the detected compounds are responsible for most of the total toxicity (Schafer et al., 2011; Lindström et al., 2015; Knauer, 2016; Munz et al., 2017).

4 Transport pathways of pesticides to surface waters

Pesticides reach surface waters along several pathways, either originating from point sources such as farmyard runoff or wastewater treatment plants, or as diffuse losses due to spray drift and atmospheric deposition, surface runoff and leaching to field drains or to shallow groundwater (Figure 1). Pesticide losses originating from point sources and contributions from spray drift and atmospheric deposition were not studied in the work presented in this thesis, and will therefore only be briefly presented in Sections 4.1 and 4.2 below. The remaining text will focus on transport occurring at the soil surface and through the soil profile (surface runoff, drainage and sub-surface saturated flow). These pathways, their effects on surface water quality and the factors affecting their occurrence and relative importance under different conditions are described in more detail.

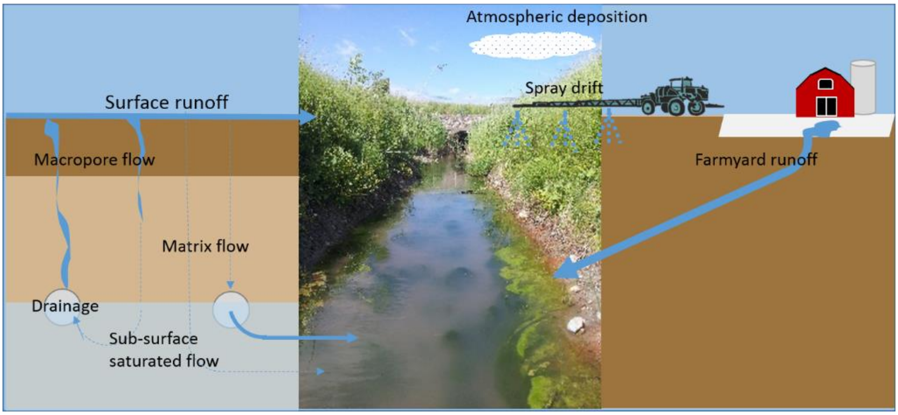

Figure 1. Schematic figure depicting the main transport pathways for pesticides from agricultural land to surface waters.

4.1 Point sources

Point sources of pesticides entering surface waters include runoff from hard surfaces in farmyards due to faulty equipment, improper waste disposal and accidental spills or carelessness during filling and cleaning operations etc. (Kreuger, 1998) and wastewater treatment plants and sewage overflows (e.g. Gerecke et al., 2002; Neumann et al., 2002). In their review of studies from several European countries, Holvoet et al. (2007) found that point sources accounted for 20-80% of total pesticide loads to surface waters. Following a controlled herbicide application in a small Swiss catchment, Leu et al. (2004a) found that diffuse losses accounted for more than 80% of total herbicide losses, but that farmyard runoff caused the largest measured concentrations. Kreuger (1998) also measured large concentrations of a number of compounds in farmyard runoff, but found that the effect on pesticide concentrations in the stream was small, suggesting that this type of contribution was rare in the catchment as a whole. However, later work revealed that point sources might have been responsible for as much as 90% of the pesticide losses to the stream (Kreuger and Nilsson, 2001). Although pesticide concentrations in the effluent from wastewater treatment plants can generally be expected to be small due to extensive dilution (Neumann et al., 2002), elevated concentrations have been found downstream of such plants (Munz et al., 2017).

Point sources can be minimized by implementing “best management practices” (as demonstrated by Kreuger and Nilsson, 2001). Cleaning the spray tank in the field instead of on hard surfaces on farmyards, regular checking and maintaining of spraying equipment and safe disposal of used pesticide containers are examples of good management practices that have great potential to reduce farmyard runoff (Reichenberger et al., 2007). Increasing the temporary storage capacity of sewage treatment plants to avoid overflows could also significantly reduce the negative impact on downstream water quality in some cases (Neumann et al., 2002).

4.2 Spray drift and atmospheric deposition

Spray drift occurs at the time of pesticide application in the field, where a part of the dose may be transported with wind and deposited on surface water. Pesticides can also be transported with wind after volatilization and deposited far away from the site of application. Although pesticides are frequently detected in rainwater (e.g. Sjöberg et al., 2011), the contribution from atmospheric deposition to pollution loads and concentrations in surface waters is, in most situations, small compared with other entry routes. I will therefore focus on losses through spray drift in the following.

The extent of spray drift is largely controlled by meteorological and technical factors. Drift has been found to increase with increasing wind speed, decreasing relative air humidity and increasing air temperature (Arvidsson et al., 2011). Spraying height, driving speed and the design and spacing of spraying nozzles also affect the extent of spray drift losses (Hilz and Vermeer, 2013). Arvidsson et al. (2011) measured average total drift losses of 5% of applied amounts for several different spray technologies and a range of meteorological conditions, of which about one quarter on average was deposited on the ground within 5 m from the end of the spraying boom in the downwind direction. Schulz (2001) showed that spray drift increased the concentrations of the two insecticides azinphos-methyl and endosulfan in a South-African catchment dominated by orchards, but found surface runoff to have a far greater effect on both peak concentrations and loads. In a small catchment in France dominated by vineyards, Lefrancq et al. (2014) found that the loads of fungicides transported in runoff increased due to spray drift deposition on roads where runoff coefficients are generally much larger.

Various technological solutions as well as mitigation strategies to minimize these problems have been developed, including drift reducing nozzles and spray additives to coarsen the spray, as well as the installation of wind-breaks and no-spray zones close to open water courses etc. (Reichenberger et al., 2007).

4.3 Surface runoff

Pesticides can be transported in surface runoff either dissolved in the aqueous phase, or adsorbed to eroded soil particles entrained in the flow. Surface runoff either results from infiltration-excess (Hortonian overland flow) or saturation-excess (Dunne type overland flow; Dunne and Black, 1970). Saturation-excess overland flow occurs when shallow water tables reach the soil surface during extended periods of snowmelt or rainfall. This is most likely to develop at the foot of hillslopes close to streams. Dense, impermeable horizons or impermeable rock at shallow depth dramatically reduces the storage capacity of the soil and increases the risk of saturation-excess overland flow. Contrasting structure and hydraulic conductivity of different soil layers can also lead to rapid lateral subsurface runoff on sloping land (Haria et al., 1994; Peyrard et al., 2016).

Infiltration-excess runoff occurs when the rainfall intensity exceeds the local infiltration capacity and depression storage capacity of the soil. Loss of particle-bound pesticides in surface runoff can be expected to be larger on steeper and longer slopes, as soil erosion is generally more extensive under such conditions. However, slope angle should not influence the generation of surface runoff per se, although it can influence the probability of runoff reaching surface water through increased flow velocity and effects on the connectivity of overland flow pathways to streams. High surface connectivity increases the area of the upslope land contributing to runoff and thus increases flow depth. Large or small scale topographic barriers may prevent flows generated at the soil surface from directly reaching the receiving surface water body. Several studies have shown that large parts of catchments may lack connectivity with the streams across the surface (as much as 66-96%; Richards and Brenner, 2004; Frey et al., 2009; Doppler et al., 2012). In these areas, surface runoff water will accumulate and infiltrate in topographic depressions. Infiltration under such ponded conditions, a process termed focused recharge, has been shown to increase leaching of pesticides to groundwater (Hancock et al., 2008) and in artificially subsurface drained areas the same effect could be expected on losses through drainage. Focused recharge is likely to occur commonly in landscapes shaped by the last glaciation, where the topography is often hummocky. Experimental studies have given contradictory results concerning the effects of slope on surface runoff (e.g. Chaplot and Le Bissonnais, 2003; Assouline and Ben-Hur, 2006). Surface runoff and associated losses of pesticides to surface water have been reported from relatively flat areas (Walton et al., 2000; Otto et al., 2012) that would be typical for a significant proportion of the Swedish agricultural landscape.

Insufficient infiltration capacity often arises from poor soil structure resulting from compaction by, for example tractor wheels, or from aggregate breakdown, sealing and crusting. Especially silty soils with low clay and organic matter content are prone to structural degradation due to low aggregate stability and a propensity for soil surface sealing and crusting (Le Bissonnais et al., 1995; Gronsten and Borresen, 2009). Both clay content and soil organic matter, in addition to precipitated sesquioxides and carbonates, generally increase soil structural stability and thereby the degree of aggregation, although there is some variation induced by differences in clay mineralogy and the composition of soil organic matter (Bronick and Lal, 2005). Although some of the properties of the soil that determine the dominant form of runoff are relatively stable (e.g. soil texture), considerable temporal variations in soil structural and therefore hydraulic properties occur in agricultural fields (Mapa et al., 1986; Moret and Arrue, 2007; Alletto and Coquet, 2009; Schwen et al., 2011). Changes in soil structure at or close to the soil surface, and thus infiltration rates, surface roughness and detention storage, result from the interactions of a number of structure forming and degrading processes. Among such are tillage and traffic events, faunal and plant root activity, swelling and shrinkage arising from wetting and drying cycles as well as freezing and thawing in cold climates (Fiener et al., 2011). Soil sealing resulting from the breakdown of unstable soil aggregates due to rainfall usually only affects a thin layer at the surface, but can significantly reduce the infiltration capacity (Assouline, 2004). These changes may dramatically change the partitioning of rainfall between surface runoff and infiltration. Better characterization and identification of the main drivers could help identify suitable ways of incorporating such processes in pesticide fate models.

Pesticide losses in surface runoff are largest when heavy rainfall occurs within a few days after application, and concentrations usually decrease with time after the first few runoff events (Burgoa and Wauchope, 1995). With time, pesticides are degraded by soil microbes and leach below the shallow "mixing zone" close to the soil surface, whereby they become less available for transport in overland flow. Otto et al. (2012) found that about 99% of the total herbicide load transported with surface runoff from a gently sloping field over three growing seasons was attributable to two extreme rainfall events with high intensities and in one case also long duration. In both cases, these were the first rainfall events that occurred after pesticide application.

Surface runoff has often been assumed to dominate pesticide transport to surface waters, or to cause the most critical events in terms of risk to aquatic ecosystems (e.g. Capel et al., 2001; Schriever and Liess, 2007). Burgoa and Wauchope (1995) reviewed studies on pesticide losses in surface runoff and concluded that in most cases total losses are below 0.5% of the total applied mass, but that much larger losses (up to 48%) can occur in extreme cases. Capel et al. (2001) collated results from similar studies and found 90th percentile losses from individual fields ranging between 0.47 and 23% of applied amounts. The authors however cautioned that the unrealistically high simulated rainfall rates often applied in irrigated plot-scale studies may overestimate losses under natural conditions in the field.

4.4 Drainage

Artificially improving the internal drainage in soil is a commonly adopted agronomic practice in many parts of the world where excess water causes problems with soil trafficability, root respiration or surface runoff and erosion. Common forms of artificial drainage include subsurface systems such as permanently installed pipes or periodically regenerated mole drains and surface systems such as drainage ditches and surface inlet wells. Artificial drainage systems are installed to reduce problems associated with excessive soil moisture, and thus, if functioning properly, can be expected to reduce losses of pesticides through surface runoff (Brown et al., 1995a; Kladivko et al., 2001), although losses through drainage would increase. The drainage intensity, partly determined by the spacing of drains and the efficiency of the system in rapidly conducting collected drainage to the ditch or stream may have a great influence on the magnitude of losses (Kladivko et al., 1991; Jones et al., 2000).

Pesticide leaching to drains in fine-textured soils is dominated by preferential transport through soil macropores (cracks, earthworm burrows and root channels; Jarvis, 2007) as demonstrated in several field-scale studies (Haria et al., 1994; Brown et al., 1995b; Johnson et al., 1996). Brown and van Beinum (2009) also found that both the concentration and total losses of pesticides through drainage were positively correlated with soil clay content in their review of studies from a number of European countries. However, preferential transport to drains also occurs in lighter-textured loamy soils (Kladivko et al., 1991; Zehe and Fluhler, 2001; Riise et al., 2004). The effects of preferential flow and transport occurring in macropores are dependent on the profile-scale connectivity of such "highways". By blowing smoke into drainage pipes, Shipitalo and Gibbs (2000) demonstrated that only macropores located right above or in close vicinity of the pipes were directly connected with the drainage system and were therefore expected to contribute to rapid transport. The strength of preferential flow has also been demonstrated to increase when such paths are mainly connected in the direction of flow (i.e. downwards in the unsaturated zone) and exchange in the horizontal direction (i.e. with the less permeable matrix) is limited (Jarvis et al., 2016). Such anisotropic structure is presumably much more common in subsoils than in topsoil, but may also occur in more shallow soil horizons due to poor structural development or, for example, compaction by heavy machinery.

Both field studies (e.g. Jones et al., 2000; Brown and van Beinum, 2009) and numerical model simulations (Nolan et al., 2008; Lewan et al., 2009) demonstrate that concentrations and loads transported in drainage are sensitive to the time elapsed between application and the first rainfall event that triggers drainage. As for surface runoff, the largest concentrations and the majority of the total pesticide transport in drainage generally occur during the first significant discharge events following application and then decline with time (Kladivko et al., 2001). Longer timespans allow more degradation to occur and increase the probability that pesticides move into the soil matrix, thereby becoming less available for transport through macropores to subsurface drains. Experiments on soil blocks conducted by Shipitalo et al. (1990) demonstrated that a small, low-intensity rainfall preceding heavier storms can substantially reduce the transport of surface-applied compounds through macropores.

In their review of European studies of pesticide transport to surface water through drainage, Brown and van Beinum (2009) found seasonal losses of pesticides ranging from not detectable to above 10% of the applied dose, which is similar to results reported in American studies reviewed earlier by Kladivko et al. (2001). Although several studies, predominantly conducted at the plot and field scale, have found larger pesticide concentrations and/or loads transported in surface runoff than in drainage (e.g. Buttle and Harris, 1991; Haria et al., 1994; Brown et al., 1995a; Chretien et al., 2017), other studies have demonstrated the opposite. Riise et al. (2004) measured similar or slightly larger peak concentrations of propiconazole and bentazone in drainage than in surface runoff from two field sites in Norway (silty clay loam and silty loam soils), and also found that the total amounts transported through drainage were larger. The rapid breakthrough of the two pesticides and a bromide tracer applied at the same time were attributed to transport through soil macropores. Similar findings were reported by Johnson et al. (1996) on a mole-drained cracking clay soil in the UK. Flows initiated as surface runoff may also reach recipient surface water bodies predominantly as subsurface drainage via surface drain inlets or as focused recharge from surface depressions to shallow groundwater, as observed by Doppler et al. (2012) in a small Swiss catchment.

4.5 Saturated subsurface flow (base-flow)

Between storm events the water flowing through streams is delivered through intrusion of shallow groundwater. Although there are studies that have documented pesticide occurrence in streams during these base-flow conditions (e.g. Squillace et al., 1993; Petersen et al., 2012) as well as in groundwater aquifers with potential exchange with streams (Kolpin et al., 2001), few attempts at comparing contributions from this pathway to those from others appear to have been made. The general view, however, seems to be that contributions from base flow and groundwater are mostly small, and that pollution of surface waters with pesticide mainly occurs as isolated events associated with increased runoff due to heavy rainfall or as the result of point-source pollution. However, although stream concentrations of pesticides can be expected to be smaller under base-flow conditions (e.g. Petersen et al., 2012), intrusion of contaminated groundwater may cause chronic low-dose exposures that can be harmful to aquatic ecosystems. Also, as recently suggested by McKnight et al. (2015), groundwater may be an important contributor of legacy pesticides, some of which may be toxic to aquatic organisms at small concentrations. The latter authors found a large number of banned or discontinued compounds in Danish streams during base-flow conditions, in some cases at concentrations that were larger than during rainfall-induced runoff events.

5 Effects of agronomic practices on pesticide transport to surface waters

Agronomic practices including the types of crops and cropping systems, tillage systems, artificial drainage and the type and amounts of pesticides applied at different times affect the risks of losses of pesticides to surface waters. Different crops develop at different rates and cover the ground to variable extents at different times, which affects the risk of soil sealing and thereby surface runoff (Fiener et al., 2011). Temporal variation in the amount of water removed from the soil through evapotranspiration furthermore affects soil wetness. Pesticide usage also varies greatly between different crops due to differences in sensitivity to various insect pests and diseases, relative competitiveness with weeds, the balance between pesticide prices and return on produce etc. This results in variable spatio-temporal patterns of pesticide applications which determine the amount of pesticides that are available for transport during rainfall events. The intrinsic properties of a compound, such as its vapour pressure, persistence in soil, adsorption to organic carbon and mineral surfaces and water solubility, strongly affect its fate and behaviour in the environment. The risk of off-site transport of more rapidly degraded and/or more strongly adsorbing compounds is generally expected to be smaller than that for more persistent and mobile ones. Brown and van Beinum (2009) found correlations between pesticide concentrations and total losses in drainage and both dissipation half-life in soil (DT50) and the organic carbon partitioning coefficient (K_{oc}). Compound properties may also influence susceptibility to transport in fast surface and subsurface flow pathways. For example, mobile weakly adsorbing compounds may diffuse into aggregates more quickly and to a greater extent than more strongly adsorbing ones. Such “protection” in small intra-aggregate pores makes more mobile compounds less susceptible to transport with surface runoff (Burgoa and Wauchope, 1995) and macropore flow to drainage systems (Larsson and Jarvis, 1999). Strongly adsorbing compounds, i.e. those that have

K_{oc} values larger than about 1000, are predominantly transported bound to eroded soil particles. Such transport is expected to mainly occur as a result of surface runoff due to the greater shear stress and carrying capacity of rapidly flowing water. However, colloidal transport in macropores may also contribute to losses of strongly adsorbing pesticides through drainage (Petersen et al., 2002; Gjettermann et al., 2009; Kjaer et al., 2011).

Alletto et al. (2010) reviewed the literature on tillage effects on pesticide fate in soils. The effects of tillage on losses along both surface and subsurface pathways were found to be very sensitive to soil moisture and weather conditions. They also concluded that conservation tillage or no-till systems have generally proven effective in reducing pesticide losses through surface runoff owing to increased surface roughness and greater aggregate stability resulting from crop residues left on the soil surface. Losses to drains through macropores may however increase when their connectivity is not disrupted by tillage (Larsbo et al., 2009). The structure of tilled soils and thus the partitioning of runoff between surface and subsurface pathways is very variable in space and time. Strudley et al. (2008) concluded that the effects of tillage events on soil structure generally lead to an increase in saturated and near-saturated infiltration capacity, but that these effects rapidly diminished with time as the soil re-consolidates. In-field traffic during management operations, such as application of fertilizers and pesticides, can cause soil compaction and reduced infiltration rates in wheel-tracks, creating connected flow paths for surface runoff (Buttle and Harris, 1991; Larsbo et al., 2016).

6 Temporal variations in soil structure and hydraulic properties (Papers I and II)

Soil structure varies considerably with time in agricultural soils, as a result of complex interactions between soil management (e.g. tillage and traffic) and site-specific environmental factors. The resulting temporal variations in soil hydraulic properties significantly affect the soil water balance (e.g. partitioning between infiltration and runoff), but are still poorly understood. For example, post-tillage decreases in saturated and near-saturated hydraulic conductivities have been frequently observed (e.g. Mapa et al., 1986; Cameira et al., 2003; Alletto and Coquet, 2009; Schwen et al., 2011), although the underlying changes in the properties of the structural pore-space have not been studied. A lack of direct measurements of post-tillage changes occurring in the structural pore system currently hampers the development, evaluation and parameterization of models capable of accounting for temporal variation in soil infiltration and thus the risk of generating surface runoff.

The work presented in Papers I and II aimed at quantifying the post-tillage changes occurring in the properties of structural pores and saturated and near-saturated hydraulic conductivities, as well as to determine the effects of soil properties such as soil texture and soil organic carbon (SOC) content on these changes.

In Paper I, the temporal evolution of soil structural pore networks and saturated and near-saturated hydraulic conductivities following tillage were studied in the field, where the soil is subjected to naturally occurring climatic influences and biological processes as well as management operations. The investigated field is about 0.42 ha and it is located approximately 15 km south of Uppsala. The soil is a clay loam according to the USDA soil classification system and has an organic carbon content of 1.3%. Intact soil cores were sampled using 100 mm high PVC cylinders with an inner diameter of 68 mm. One sample was collected from each of four locations along a transect of the field, approximately 20 m apart, on each of five sampling occasions during the growing season 2013: 23rd May, 18th June, 28th June, 11th July and 15th August. X-ray tomography with a final resolution of 120 µm was used to image the structural pore systems in these soil cores. After scanning, samples were slowly pre-wetted from below before saturated hydraulic conductivities (K_s) were measured using the constant head method. At the time of sampling, near-saturated hydraulic conductivities were also measured in the field with tension disc infiltrometers at pressure heads of -1 and -6 cm close to where the soil cores were sampled. From the third sampling occasion on 28th June and throughout the rest of the study, four additional soil cores were collected from within wheel tracks that formed following pesticide spraying. Measurements of near-saturated hydraulic conductivity were also made in these wheel-tracks.

Processing and analyses of the tomography images were performed using the Fiji distribution (Schindelin et al., 2012) of the open access software ImageJ (Abramoff et al., 2004) and the GeoDict software (Math2Market GmbH, http://www.geodict.com). The imaged porosity was determined for the whole sample, as well as in the uppermost 5 mm of the soil surface and for a small cylindrical sub-volume located at the center of the soil core, between 2.5 and 5.0 cm below the average depth of the soil surface. This smaller subset of the sample was assumed to be free from sampling artifacts which might have been present close to the cylinder walls and was used to determine temporal changes occurring in the properties of the structural pore networks. The entire sample volume was analyzed in order to relate structural properties to measured K_s. The size (thickness) distribution of structural pores between the three pore size classes <0.5 mm, 0.5-3.0 mm and >3.0 mm, as well as measures reflecting their shape and connectivity were also calculated. Details of the procedures are described in section 2.2.2 in Paper I. Mixed-effects ANOVA was used to determine the effects of time and wheel traffic on the measures of porosity and pore morphology as well as near-saturated and saturated hydraulic conductivity. Correlation analyses using the non-parametric Spearman rank test were also performed for spore space measures and hydraulic properties. All statistical analyses were performed with the open access software R (R CoreTeam, 2014).

Between the first sampling occasion one week after harrowing (23rd May) and the second sampling around three weeks later (18th June) a number of rainfall events occurred with a maximum of 15 mm falling in one day. The imaged porosity both at the soil surface and in the small sub-volume decreased between these dates (Figure 2), but the difference was only significant for the soil surface ($p = 0.003$).

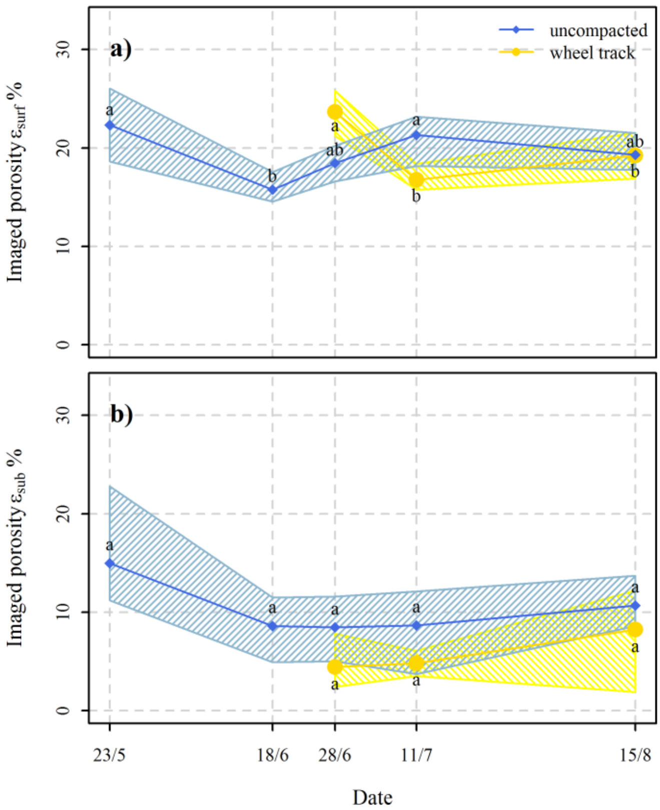

Figure 2. Temporal evolution of imaged porosity in a) the uppermost 5 mm of the soil surface and b) the cylindrical sub-volume (2.5-5.0 cm depth) at the center of the sampled soil core following harrowing for uncompacted soil and from within wheel tracks. Different letters indicate statistically significant differences between means over four replicates ($p < 0.05$) and the shaded area shows the range of measured values.

The decrease in porosity at 2.5-5.0 cm depth occurred mainly through a loss of pores larger than 0.5 mm (Figure 4 in Paper I), although as for total imaged porosity at this depth, this difference was not significant ($p = 0.069$). The loss of porosity also appeared to have affected the connectivity of the pores. The percolating porosity, which is defined as the porosity constituted by continuous pore clusters that connect the top and the bottom of the sample, decreased (Figure 5a in Paper I). The change was, however, not significant.

No significant temporal changes were found in K_s measured on the samples in the laboratory, which was characterized by a large spatial variability. In contrast, unsaturated hydraulic conductivity at pressure heads of -1 and -6 cm measured in the field decreased by around one order of magnitude ($p = 0.039$ and 0.016, respectively; Figure 3).

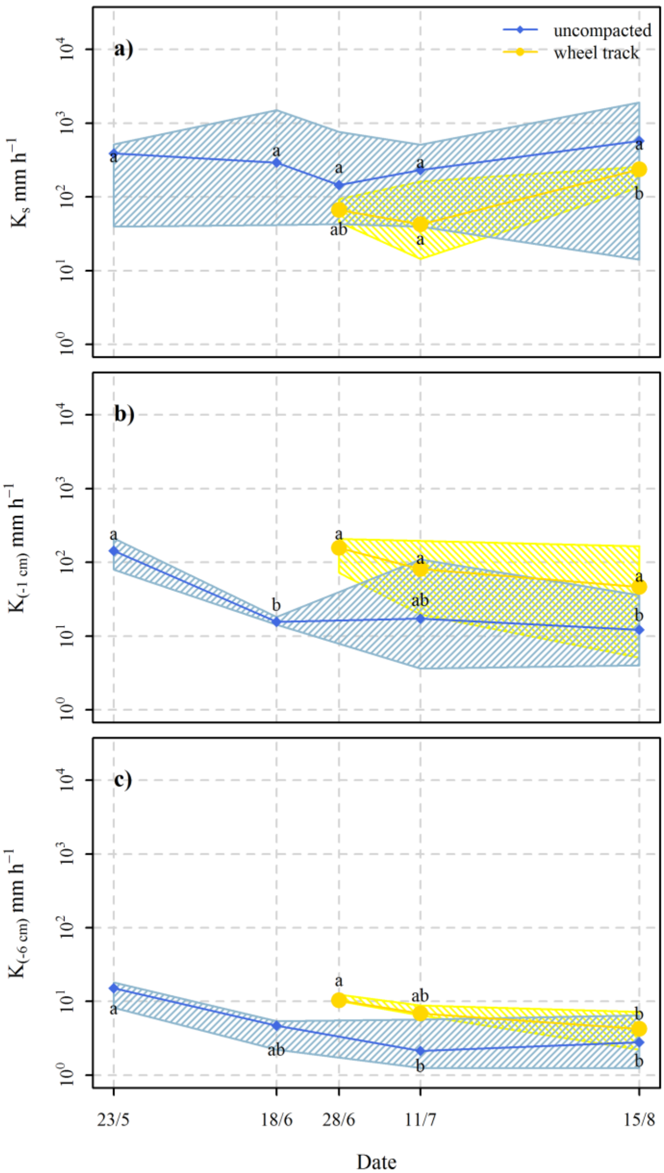

Figure 3. Temporal evolution of a) saturated hydraulic conductivity measured on the imaged soil cores in the laboratory and near-saturated hydraulic conductivity measured with tension-infiltrometers in the field at supply pressures of b) -1 cm and c) -6 cm. Different letters indicate statistically significant differences between means over four replicates ($p < 0.05$) and the shaded area shows the range of measured values.

The most striking and somewhat surprising effect of traffic on soil structure and hydraulic properties was that both soil surface porosity (Figure 2a) and near-saturated hydraulic conductivity at both pressure heads (Figures 3 b and c) were larger in wheel tracks than in uncompacted soil on the sampling occasion immediately following the traffic event. The likely explanation for these results is that a soil crust formed following the rainfall events between 23rd May and 18th June, which was broken up by the tractor wheels. This suggests that structural changes resulting from natural processes occurring in the field may sometimes have a greater effect on infiltration rates at the soil surface than changes induced by agricultural practices. However, Larsbo et al. (2016) measured runoff of pesticides in the same field in the three consecutive years between 2012 and 2014. In this study, surface runoff only occurred during the growing season in 2012 and was then only generated in wheel tracks. Inter-annual variation in precipitation patterns as well as the soil water content at the time of traffic events can thus be expected to have a strong influence on the effects of both surface sealing and traffic-induced compaction on soil infiltration.

K_s was most strongly correlated ($\rho = 0.5$, $p = 0.035$) with a measure of pore connectivity – the connectivity probability Γ – which is defined as the likelihood that any two imaged pore voxels belong to the same cluster, i.e. that they are connected. It is calculated as:

$$\Gamma = \frac{1}{{n_p}^2}\sum_{i=1}^{N} {n_i}^2 \qquad (1.)$$

where N is the number of pore clusters in the sample, n_p is the total pore volume in the sample (expressed as the number of voxels), and n_i is the volume (in voxels) of pore cluster i. This measure was also strongly correlated with total imaged porosity of the sample ($\rho = 0.85$, $p << 0.001$). Strong correlation between total porosity and pore space connectivity have also been found by Schäffer et al. (2007) and Jarvis et al. (2017). Despite the correlation between K_s and Γ and the strong correlation between Γ and imaged porosity, no correlation was found between total imaged porosity and K_s (Figure 8 in Paper I). In contrast, several other studies have found imaged porosity to be a good predictor of K_s (Udawatta et al., 2008; Kim et al., 2010; Luo et al., 2010). The lack of correlation between K_s and any of the measures reflecting the largest pores, as well as the lack of temporal changes in K_s despite the observed changes in the volume and size distribution of structural pores, may have resulted from experimental artifacts introduced during pre-wetting of the samples at the laboratory. Recently harrowed soil can be expected to be structurally unstable upon wetting, and it is thus possible that structural changes occurred in the samples between X-ray scanning and conductivity measurements. It is also possible that entrapped air blocked the larger passages through the pore system (Dohnal et al., 2013; Snehota et al., 2015), thereby obscuring the expected relationship between K_s and structural porosity. In addition to the connectivity probability Γ, K_s was also moderately correlated with the critical pore diameter ($\rho = 0.40$, $p = 0.049$), which is defined as the thickness of the largest sphere that can fit into a continuous pore connecting the top and bottom of the sample, and also with the porosity <0.5 mm ($\rho = 0.39$, $p = 0.005$; Figure 8 in Paper I). The critical pore diameter was small on all sampling dates (figure 5b in Paper I), indicating that the connectivity of pores larger than 0.5 mm were generally limited. Since temporal changes were only observed in the two larger pore size classes, this may, in addition to the mentioned experimental artifacts, explain the lack of significant temporal changes in K_s.

The changes that occurred in the porosity between 2.5 and 5.0 cm depth (Figure 2b) and in the percolating porosity (Figure 5a in Paper I) following the first rainfall events were not statistically significant even though they were quite large with barely overlapping ranges. Large spatial variation, in combination with the small number of replicate samples dictated by the time-consuming nature of image processing and analyses, hampered the ability to quantify temporal changes in soil structural porosity in the field.

Thus, to limit spatial variation, in Paper II, experiments were undertaken in the laboratory, where repeated measurements were made on the same samples during a sequence of wetting and drying cycles in order to study post-tillage soil consolidation and surface sealing. Measurements were made on nine different soils with contrasting particle size distribution and soil organic carbon content in order to determine the effects of soil properties on post tillage structural changes.

Samples were collected in spring 2015 from the recently harrowed layer of nine fine- and medium-textured Swedish soils at five different sites (one of them being the site studied in paper I). These soils comprised three clay soils, four clay loam soils and two silt loam soils with SOC contents varying between 1.2 and 4.0%. More information about the sites and soils is presented in Table 1, where soils are listed according to clay content. Three replicate samples were prepared for each soil by filling PVC cylinders (68 mm inner diameter, 100 mm high) sealed at the bottom by polyamide mesh and gently shaking them to make the soil settle. These samples were then first slowly pre-wetted through capillary rise for five days before equilibration of the water content at a pressure head of -30 cm on a sand bed. Samples were scanned by X-ray tomography, as in Paper I, both before wetting and after equilibration. They were then subjected to three cycles consisting of one irrigation with simulated rainfall at an intensity of 5 mm h^{-1} for 4 hours followed by equilibration at -30 cm on a sand bed for five days

Table 1. *Properties of the nine soils investigated in Paper II*

Soil	Sampling location	Coordinates	Soil type (USDA)	Clay content (%)	Silt content (%)*	Sand content (%)	SOC (%)
S3	Säby	59°50'24"N; 17°42'7"E	Clay	57.3	38.5 (28.7)	4.2	2.4
U3	Ultuna	59°49'33"N; 17°39'34"E	Clay	54	26.1 (21.4)	19.9	1.5
U2	Ultuna	59°48'46"N; 17°39'9"E	Clay	50.7	37.6 (27.6)	11.7	1.2
S2	Säby	59°50'1"N; 17°42'8"E	Silty clay loam	35.1	58.8 (27.1)	6.1	3.3
K	Krusenberg	59°43’60”N; 17°41’21”E	Clay loam	33.7	32.4 (19.4)	33.9	1.4
S1	Säby	59°50'14"N; 17°42'35"E	Silty clay loam	32.2	58.2 (21.8)	9.6	2.5
U1	Ultuna	59°49'24"N; 17°38'42"E	Sandy clay loam	23.2	17.5 (11.7)	59.3	1.2
Å	Ålbo	59°55'49"N; 16°18'33"E	Silt loam	21.5	66.6 (52.8)	11.9	1.6
R	Röbäcksdalen	63°48'27"N; 20°14'21"E	Silt loam	7.1	74.7 (25.8)	18.2	4

*% fine silt (2-20 µm) given within parenthesis.

and then scanning.Image processing and analyses were performed using ImageJ and R. The porosities of the whole sample and the uppermost millimeter closest to the soil surface were calculated, as well as the size distribution of pores in four classes (<60, 60-600, 600-1200 and >1200) and two measures of the connectivity of the imaged pore space (the connectivity probability and the percolating fraction). The measured pore size distributions (PSD) were fitted by least-squares regression to a power law model with two parameters, the maximum pore size, d_{max}, and an exponent, λ, that reflects the spread or distribution of pore sizes:

$$V_f = \left(\frac{d}{d_{max}}\right)^{\lambda} \quad (2.)$$

where *d* is pore diameter (thickness) and V_f is the fraction of the pore volume that has a thickness smaller than *d*. This model is equivalent to Campbell’s (1974) equation for the water retention curve.

Repeated-measures ANOVA was used to test the statistical significance of differences between the means of measured variables at different stages of the experiment. Pearson correlation coefficients for linear relationships between relative changes in sample and soil surface porosities, soil particle size classes and SOC were calculated to investigate the effect of soil properties on the magnitude of changes occurring over the course of the experiment.

Structural changes occurred in all soils in response to the wetting and drying cycles that they were exposed to, but the effects on total and surface porosity, PSD and connectivity of larger structural pores varied greatly between soils. Total porosity decreased in all soils except for the two clay soils U3, where total porosity increased by about 3%, and soil U2 where it remained unchanged (see Figure 2 in Paper II). In the remaining soils, total porosity decreased by 2-24%, with the largest change occurring in the silty soil with low SOC (1.6%; soil Å).

Large changes in the PSD occurred in the two clay soils U3 and U2 as well as in the three clay loams S2, K and S1. In these soils, there were pronounced shifts towards a larger proportion of smaller pores. A smaller change in the same direction also occurred in one of the silty soils (soil R). The power law model fitted to the PSD (Figure 4) generally described the data quite well, with R^2 values ranging from 0.86 to more than 0.99, with a median value of 0.99. The exponent λ describing the slope of the curve decreased significantly after the initial wetting in the two clay soils U3 and U2 (by 0.077 and 0.098, respectively) as well as in the three clay loams S2, K and S1 (by 0.054, 0.091 and 0.077, respectively), reflecting a shift in pore thicknesses from larger to smaller pores.

The largest relative changes in both total porosity and the PSD occurred after the initial wetting and equilibration, but the cumulative change in total porosity after all three irrigation events were generally of similar magnitude or even larger (Figure 3 in Paper II). Decreases in total porosity and especially the volumes of larger structural pores also led to decreases in the connectivity of imaged porosity in the clay soil U3 and the clay loam soils S2, K and S1 (Figure 6 in Paper II). Connectivity remained high, however, in all soils, and even increased in the silty soil Å and the sandy clay loam soil U1 due to crack formation upon drying.

Large decreases in soil surface porosity occurred in the two silty soils Å and R (Figure 7 in Paper II). At the end of the experiment, surface porosity had decreased by 75 and 73% to 0.11 and 0.12 $cm^3 cm^{-3}$, respectively, which was smaller than in any of the other soils, which had final surface porosities of 0.17-0.24 $cm^3 cm^{-3}$. In Å, large decreases occurred both during wetting and equilibration and during the first irrigation event (relative decreases of 55 and 45%, respectively), whereas surface porosity only decreased during the first irrigation event in R. This difference in temporal dynamics likely reflects the

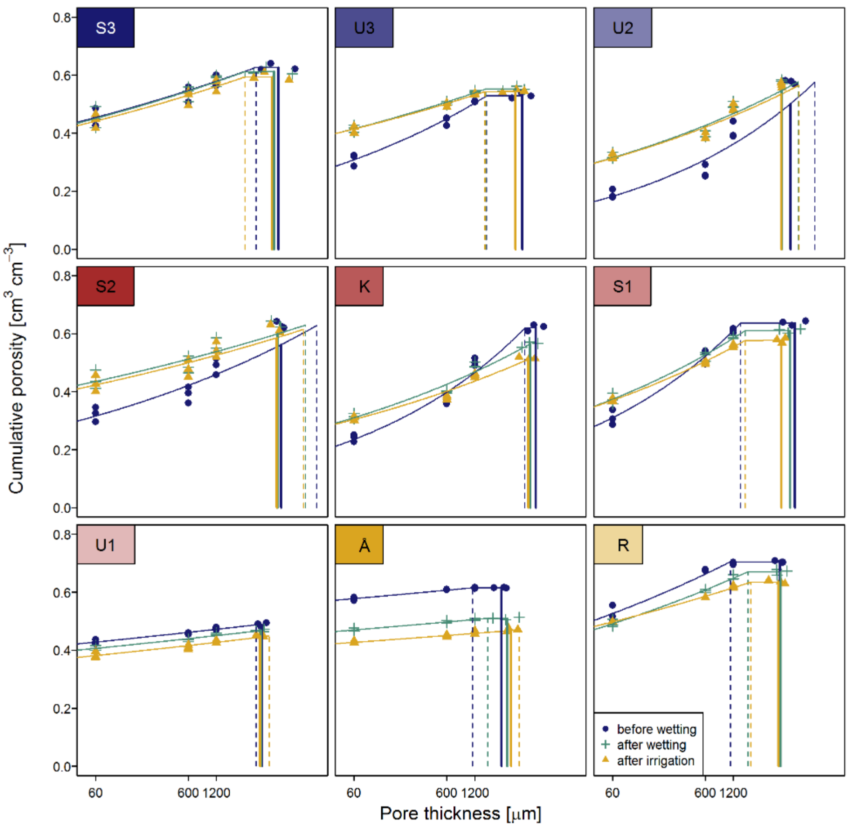

Figure 4. Equation 2 fitted to the pore size distributions of each soil before wetting, after wetting and equilibration and after three four hour irrigations. Solid vertical lines indicate the measured maximum pore thickness (mean of three replicates) and dashed vertical lines mark the estimated maximum pore thickness.

difference in SOC content between these two silty soils (1.6 and 4.0%, respectively), resulting in weaker aggregates in Å and reduced stability during wetting (LeBissonnais, 1996; Gronsten and Borresen, 2009). In addition to increasing aggregate strength, SOC induces hydrophobicity which reduces the wetting rate and thus decreases the risk of slaking, i.e. aggregate disruption due to pressurized air entrapped during fast wetting (Bronick and Lal, 2005; Blanco-Canqui and Benjamin, 2013).

The changes occurring in soil surface porosity ($\Delta\varepsilon_{surf\ (w+ir)}$) were strongly and negatively correlated with soil silt content (r = -0.81, R2 = 0.65, p = 0.009; Figure 5). This result is in line with the large propensity for soil surface sealing and crusting, surface runoff and erosion that is associated with primarily silty

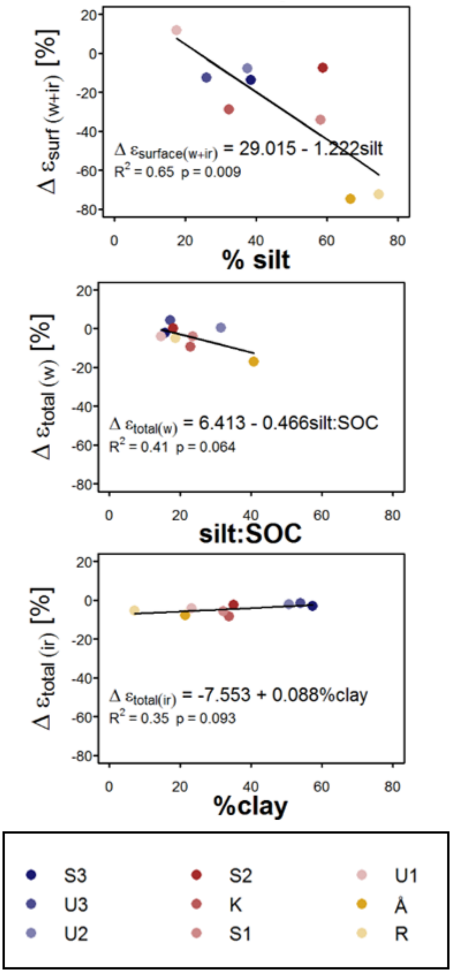

Figure 5. Relationships and linear correlations between the changes that occurred in soil surface porosity over the course of the entire experiment (Δεsurf (w+ir)), and total porosity after the initial wetting and equilibration (Δεtotal (w)) and after the three 4 hour irrigations (Δεtotal (ir)) and soil texture and SOC variables that were found to be significant at $p < 0.1$.

soils due to their low structural stability (Le Bissonnais et al., 1995; Barthes and Roose, 2002; Gronsten and Borresen, 2009). Weak correlations (at $p < 0.1$) were found between the changes in total porosity after the initial wetting ($\Delta\varepsilon_{total\ (w)}$) and the ratio of silt to SOC content (silt:SOC; $\rho = -0.64$, $R2 = 0.41$, $p = 0.064$) and the changes in total porosity after irrigation ($\Delta\varepsilon_{total\ (ir)}$) and clay content ($\rho = 0.59$, $R2 = 0.35$, $p = 0.093$). In contrast, the changes in λ were very strongly positively correlated with its initial value ($r = 0.82$, $R2 = 0.90$, $p < 0.001$). The PSD in the harrowed layer, and in particular the volume and size distribution of large inter-aggregate pores, can be expected to be largely determined by the aggregate size distribution, which in turn is strongly affected by other site-specific factors like soil management history, tillage practices and the soil water content at the time of tillage (Dexter, 1979). Despite weak or lacking correlation between soil texture and the changes in total porosity and the PSD, responses to the experimental wetting and drying cycles were broadly similar within the broad soil texture groups (clay soils, clay loam soils and silty soils). Measurements performed on a larger number of soils would allow development of stronger statistical relationships between structural changes, soil texture and SOC.

A number of different processes contribute to post-tillage structural changes. Aggregate coalescence (plastic deformation) due to capillary forces induced by drying was likely the dominant process leading to the decreases in total leading to the decreases in total porosity and shifts of the PSD towards smaller pore sizes that were observed in the three clay loam soils S2, K and S1. A mechanistic model describing such changes has been presented by (Ghezzehei and Or, 2000; Or and Ghezzehei, 2002). Accounting for swelling (and shrinking) as well, which likely occurred in the two clay soils U3 and U2 where the PSD shifted towards larger proportions of smaller pores while total porosity increased slightly or remained unchanged, would make such models more generally applicable. Post-tillage structural evolution could also be modelled as changes in total porosity and the PSD, as suggested by (Or et al., 2000). The advantage of this simpler approach is that the underlying processes resulting in structural changes do not need to be specifically known and modelled. The exponential model fitted to the PSD of the nine soils that were studied in Paper II described the data rather well, suggesting that it would be feasible to model post-tillage changes as changes in the pore size distribution index λ, the maximum pore size and total porosity.

7 Spatial variation in pesticide losses to an agricultural stream as affected by variation in soil properties (Paper III)

At the larger spatial scales which are most relevant for risk assessment and mitigation, the application of detailed simulation models may not be feasible due to limited information on the spatial and temporal variation of important input parameters. Under these circumstances simpler, yet robust, methods for assessment of the relative risks of pesticide losses to surface waters are an attractive option. Siber et al. (2009) and Schneider et al. (2007) have shown that soil properties can be expected to be good predictors of catchment hydrology and the frequency by which fast runoff processes are triggered. Maps of soil texture are generally relatively easily obtained, and they could potentially provide farmers and extension officers with a simple "proxy" method for identification of vulnerable areas and suitable mitigation measures.

To assess whether spatial differences in pesticide losses at the catchment scale can be related to variation in basic soil properties like texture and organic matter a monitoring study was undertaken in a small Swedish agricultural catchment, catchment E21, with a large variation in soil types. Three small sub-catchments were selected within this area that differ with regard to the proportion of different soil types (Figure 6). Soil type was determined based on digital soil maps of topsoil and subsoil texture and topsoil organic matter content with a 10x10 m resolution. These maps were developed by combining proximal sensing methods with soil sampling (details are given in Section 2.1 in Paper III and in Piikki et al., 2015). A simplified version of the FOOTPRINT soil classification system (Centofanti et al., 2008; Steffens et al., 2015) was used to assign each 10x10 m grid cell to one of 22 different soil classes based on topsoil and subsoil texture and topsoil organic matter content.

One of the sub-catchments (118 ha) has a relatively large proportion of soils with high clay contents (SC_{clay}). The second sub-catchment (88 ha) has a larger proportion of coarser-textured sandy soils and no clay soils (SC_{sand}), whereas the third (242 ha) comprises a mix of soil types (SC_{mixed}) and thus constitutes an intermediate between the two other sub-catchments. Agricultural land constitutes between 87 and 92% of the area of each sub-catchment. Data on cropping patterns and pesticide usage (see Figure 2 and Table 1 in Paper III) were obtained from the Swedish national environmental monitoring program data records. Within this program annual interviews are conducted with the farmers in the catchment E21. Pesticides are predominantly applied during the growing season between April and September. Annual pesticide use is less intensive in SC_{mixed} than in SC_{clay} and SC_{sand} even though roughly the same number of compounds is applied: on average for the period 2009-2015, 0.48 kg active ingredient (a.i.) ha^{-1} $year^{-1}$ was applied in SC_{mixed} compared with 1.08 and 0.99 kg a.i. ha^{-1} $year^{-1}$ in SC_{clay} and SC_{sand}, respectively.

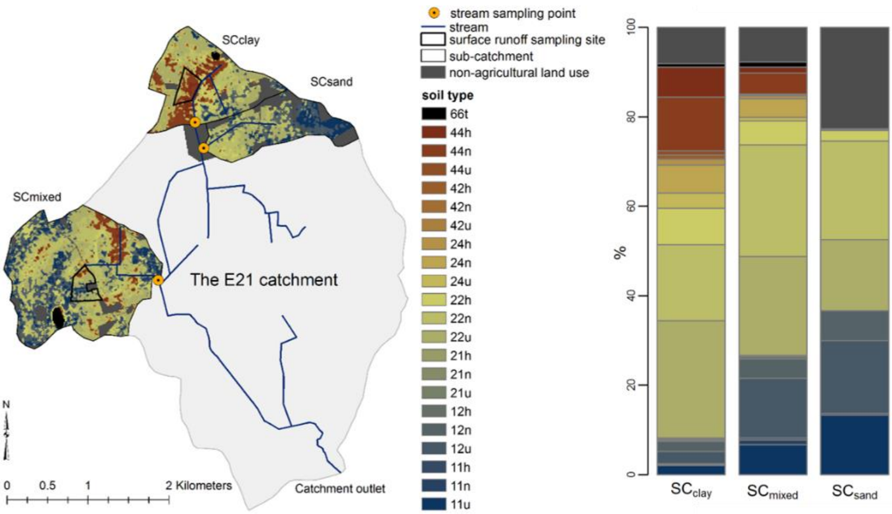

Figure 6. The catchment E21 where monitoring of pesticide concentrations in stream water, drainage and surface runoff was conducted in three selected sub-catchments SC_{clay}, SC_{mixed} and SC_{sand} during May and June in 2013-2015. The map and bar chart show the distributions of soil types, determined based on the classification scheme described in Steffens et al. (2015) in each sub-catchment. The code for soil type comprises two digits for the texture class, the first for topsoil and the second for subsoil (1=coarse soils >60% sand and <18% clay, 2=medium soils <35% clay and not coarse, and 4=fine textured soils >35% clay) and one letter for the organic matter content class (u=low <3%, n=medium 3-5%, and h=high >5%). Texture class 6 and organic matter class t denotes organic or peaty soil.

Sampling of stream water was performed at the outlet of each sub-catchment and samples were also collected from drainpipes discharging into the stream and from within-field surface runoff at two field sites in SC_{clay} and SC_{mixed} between May and June 2013-2015. Stream water and surface runoff were sampled during main runoff events using 'event-activated' passive samplers, whereas drains were sampled manually one or in some cases two or more days later. Details on sampling protocols are presented in Sections 2.2.1 through 2.2.3 in Paper III. All samples were analyzed for 99 of the most common polar and semi-polar pesticides used in Swedish agriculture using accredited methods described in Jansson and Kreuger (2010).

Clear and consistent differences in pesticide occurrence in the stream were found between the three sub-catchments. Both the number of detected compounds and the concentrations were generally larger in SC_{clay} than in SC_{mixed} (detections made in stream water samples in the three sub-catchments on each sampling occasion are summarized in Table 2 in Paper III). Only one or two compounds were found in the stream in SC_{sand} on any given sampling occasion, and then only in trace concentrations close to the detection limit (0.001-0.003 $\mu g\ l^{-1}$).

Larger proportions of applied compounds were detected in the stream in SC_{clay} than in SC_{mixed} (Figure 7). Only two of the 39 compounds that had been applied in SC_{sand} between 2009 and 2015 were detected in the stream. The spatial pattern of pesticide occurrence in streamflow strongly suggests that transport of pesticides to the stream in catchment E21 occurs almost exclusively along the faster transport pathways that can be expected to be more common in SC_{clay} and SC_{mixed} than in SC_{sand}. It also indicates that more uniform infiltration and leaching through the topsoil, which is presumably the dominant hydrological process in SC_{sand}, allowed more adsorption and degradation to occur, resulting in minimal pesticide losses to the stream. The apparent temporal stability of the observed spatial pattern suggests that soil texture maps of sufficient spatial resolution could be a useful tool for farm- and catchment-scale planning of mitigation strategies.

Figure 7 also indicates that more strongly adsorbing and/or rapidly degrading compounds were detected in stream water in SC_{clay} than in SC_{mixed}. This can be illustrated by the Groundwater Ubiquity Score (GUS), which is an index calculated based on DT50 and K_{oc} that reflects the leaching potential of a compound (Gustafson, 1989). Compounds with a GUS value smaller than 1 (very low leaching potential) were detected more frequently in the former sub-catchment: 19 detections of 7 different compounds as compared to one compound (florasulam, GUS = 0.72), which was detected on three occasions in SC_{mixed}. This indicates that transport processes may have been more rapid and potentially erosive in SC_{clay}. Fine-textured soils with high clay contents, which are more common in SC_{clay} than in SC_{mixed}, are particularly prone to preferential flow and transport through soil macropores (Jarvis, 2007). Although particle bound transport of strongly adsorbing compounds is generally associated with

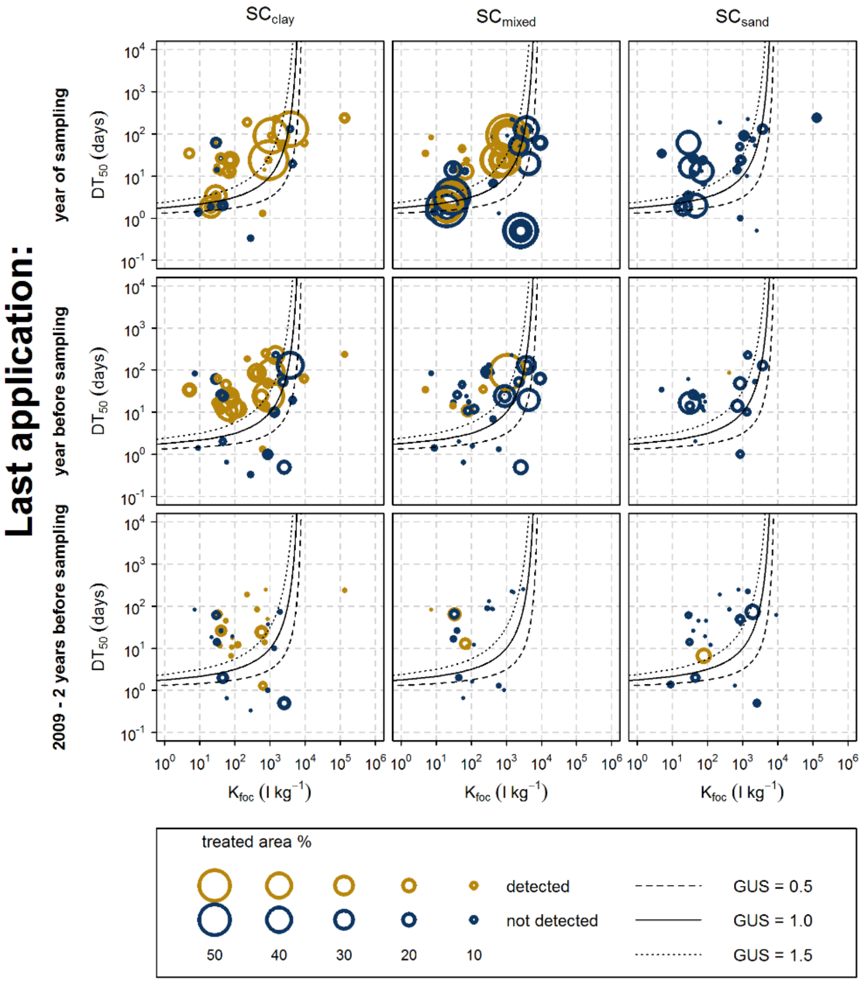

Figure 7. Compounds applied in SCclay, SCmixed and SCsand during three different time periods: the same year as sampling, the year before sampling and between 2009 and the year before sampling. Compounds are plotted according to their degradation half-life in soil (DT50) and Freundlich organic carbon partitioning coefficient (Kfoc). Pesticide properties are obtained from the Pesticide Properties DataBase (PPDB; Lewis et al., 2016). The Groundwater Ubiquity Score (GUS; Gustafson, 1989) is used to assess the leaching potential of pesticides. A GUS index value smaller than one indicates very low leaching potential. The size of symbols show the area that had been treated with each compound during the considered time period. For the period 2009 to two years before sampling the average area treated annually is considered. Gold and blue symbols indicate whether the compound was detected in the stream or not.

erosion due to surface runoff, colloidal transport to subsurface drainage systems may be another loss pathway for such compounds (Petersen et al., 2002; Gjettermann et al., 2009; Kjaer et al., 2011). Colloid-mediated transport has been found to be larger in soils with more ubiquitous macropores (de Jonge et al., 2000). The differences in pesticide occurrence in the stream between SC_{sand} and the two other sub-catchments were also reflected in samples from the drains. The only compound that was detected in drain samples from SC_{sand} was metalaxyl, a fungicide applied on potatoes. It was found on six out of nine sampling occasions in trace amounts (0.001 – 0.002 $\mu g\ l^{-1}$). Between 3 and 18 compounds were detected in samples from SC_{clay} and SC_{mixed} on any given sampling occasion. The number of detected compounds were somewhat larger in SC_{clay} (on average 8.4 as compared to 4.7), whereas the largest concentration of a single compound was found in SC_{mixed} (20 as compared to 0.51 $\mu g\ l^{-1}$).

Within-field surface runoff occurred on at least one occasion in one or both of the two sub-catchments SC_{clay} and SC_{mixed} during each sampling season. Between 4 and 13 compounds with a maximum concentration of 11 $\mu g\ l^{-1}$ were found in samples from the field in SC_{clay} and 8-21 compounds with a maximum concentration of 19 $\mu g\ l^{-1}$in SC_{mixed}.

A comparison of concentrations of the same compounds detected in both surface runoff and drainage in the same discharge event (Figure 8) shows that concentrations were larger in surface runoff. However, since the drains were sampled after the peak in discharge and likely also the peak in pesticide concentrations, the concentration difference between drainage and surface runoff during the main discharge event may have been smaller.

The extent to which surface runoff occurred and contributed to pesticide concentrations in the stream is uncertain. However, connectivity to the stream across the soil surface is very limited in this catchment (Villa et al., 2015), which has a quite hummocky topography. Furthermore, with the exception of one occasion on the 4th May 2015 (Figure 8), a consistent lack of visual signs of extensive surface runoff and erosion was noted. On this one occasion when within-field surface runoff was observed in a field in SC_{mixed}, surface water accumulated in a small depression in the field from where it re-infiltrated. Surface flows may, however, have reached the stream through surface drains connected to the sub-surface drainage systems (Doppler et al., 2012). Surface inlets are common in both SC_{clay} and SC_{mixed}. It does, however, appear as though macropore flow to subsurface drainage systems was the main transport pathway for pesticides to the stream in the studied catchment.

On all sampling occasions, a number of compounds were detected in samples from the stream in SC_{clay} and SC_{mixed}, as well as from the drains, that had last been applied in the year before sampling or even earlier. On any given sampling occasion such compounds constituted between 44 and 88% of all compounds detected in stream samples. Although some of these detections may have result-

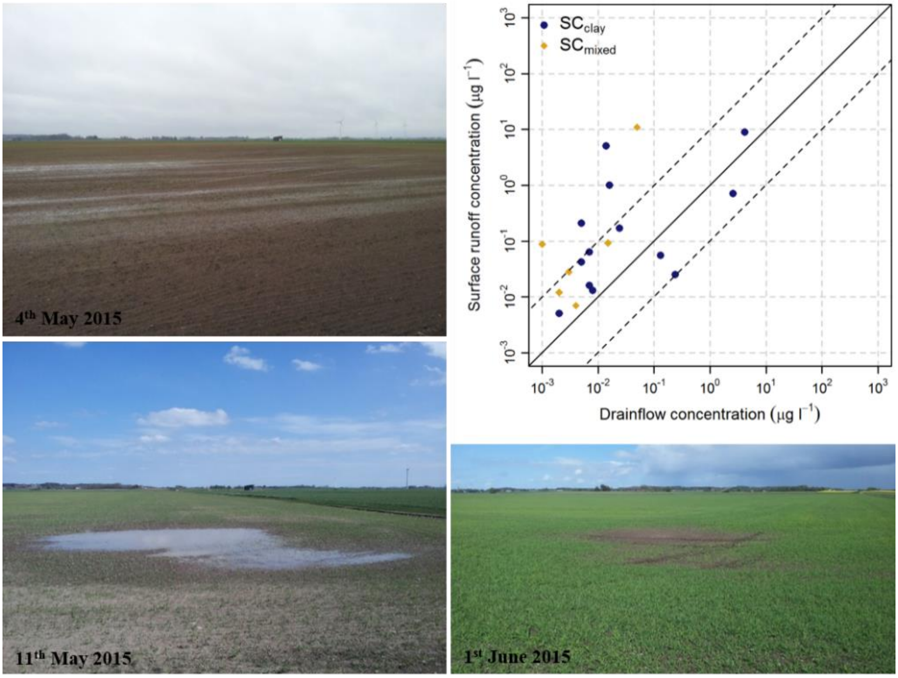

Figure 8. Concentrations in drainage and surface runoff/ponding water for concentrations that were detected in both sample types following the same discharge event. Black solid line shows 1:1 ratio and dashed lines a deviation of one order of magnitude. Photographs of within-field surface runoff observed in a field in SC_{mixed} on 4th May 2015. Water accumulated and infiltrated in a small depression in the field.

ed from unreported applications, the large number of such findings suggest that – despite the importance of fast transport pathways for pesticide losses in this catchment – the transport times from field to stream were often quite long. The likely explanation for this is that only the first part of the transport, whereby pesticides are rapidly leached below the topsoil through macropores, is fast. Slower transport to the drains then occurs, resulting either from a lack of macropore connectivity with the drains (Shipitalo and Gibbs, 2000) or insufficient duration of rainfall events to sustain macropore flow all the way to the pipes. This means that pesticides can be stored along the flow pathway, presumably in the less biologically active subsoil, for relatively long time periods before they are delivered to the stream either through drainage or saturated subsurface flows. Occurrence of compounds in streams with no recent application history have also been reported by e.g. McKnight et al. (2015) and Petersen et al. (2012).

8 Conclusions, recommendations and future research

Significant changes occur in the structural pore system of soils (total and surface porosities, the PSD and the connectivity of structural pores) following tillage as a result of natural rainfall or irrigation. The magnitude and direction of such changes vary between soils with different texture and SOC, with similar responses to repeated wetting and drying within broad groups of soils (i.e. clay soils, clay loam soils and silty soils). The propensity for surface sealing due to slaking and raindrop impact is dependent on the silt content of the soil, with soils that have high clay and SOC contents being less vulnerable. The largest structural changes appear to occur soon after tillage and then gradually decrease in magnitude as the soil approaches a more stable fully-consolidated state.

Incorporation of algorithms that account for post-tillage changes in soil structural and hydraulic properties in mechanistic models of water and solute transport in soils could be expected to lead to a greatly improved ability of such models to predict the frequency and magnitude of pesticide losses through surface runoff. This could be done by means of the changes in the total porosity, the maximum pore diameter and the slope of the PSD curve. This relatively simple approach has the advantage over more mechanistic descriptions in that the processes driving the structural changes do not need to be explicitly known and modelled. However, whether these changes are best expressed as a function of the accumulative amount of rainfall (or kinetic energy) or soil moisture variations (wetting and drying cycles) needs further investigation. The shift in the PSD is easily translated into changes in the soil water retention curve, which can in turn be related to changes in the hydraulic conductivity function, providing that the effect on K_s is known. Reliable measurement of K_s on recently harrowed structurally unstable soils using standard laboratory procedures like the constant head method is difficult, as evidenced by the pronounced structural alterations that were observed following capillary wetting in Paper II. The lack of temporal effects on K_s despite large decreases in surface and total porosity that were observed in Paper I were likely the result of experimental artefacts introduced during the measurements. Estimation of K_s from basic soil properties with existing pedotransfer functions is also fraught with uncertainty (Jarvis et al., 2016). X-ray measurements of soil pore structure and pore-scale modelling of water fluxes on such tomography images obtained during different stages of soil consolidation may offer a resolution to this challenge.

The results presented in Paper II suggest that continuous or class pedotransfer functions based on basic soil properties like texture and SOC could be used to parameterize models of post-tillage consolidation and surface sealing. However, subsequent changes in the PSD appear to be very sensitive to the structure created by tillage, which is also strongly influenced by management factors and the soil moisture content at the time of tillage. Measurements would also need to be made on a larger number of soils than the nine investigated in this study in order to develop more reliable statistical relationships between soil properties and post-tillage structural changes.

Paper III showed that at the catchment scale, losses of pesticides to the stream can vary considerably between different areas. These losses appear to be associated mostly with fine-textured soils where rapid runoff processes are triggered more frequently, primarily macropore flow to subsurface drainage systems. In the small catchment that was studied in this thesis, the spatial pattern of pesticide occurrence in the stream appeared to be stable over time. The characteristics of individual rain storms, although likely influencing the magnitude of losses, thus seem to have had a smaller influence on where losses occurred than did the intrinsic properties of the sub-catchments. This suggests that soil maps, which are readily available, could be used to locate areas that are likely to be susceptible to rapid runoff and thereby significant pesticide losses to surface water. At a national level, the importance of surface runoff relative to losses in drainage remains uncertain. Even so, soil maps should also prove useful to identify areas susceptible to surface runoff (i.e. silty soils, low in SOC). It should therefore be feasible to provide farmers and extension officers with maps delineating areas where the risk of pesticide losses along either of these pathways is particularly high, and where mitigation measures like restricted pesticide usage or vegetated buffer strips would be the most effective.

However, the extent to which it is possible to distinguish between high- and low risk areas using a simple risk index or proxy method based on soil type should be further tested under variable climate and topographical conditions, as the effects of these factors may be larger at larger spatial scales (i.e. the regional or national scale). The influence of soil properties on runoff may be weaker in catchments characterized by more pronounced topography and precipitation patterns with highly variable intensities (Schneider et al., 2007). Although this should mainly apply to southern Europe and is presumably much less relevant for most of the agricultural area in Sweden, such conditions could still occur locally.

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