Pesticides in Stream and Pond Sediments of the Vemmenhög Area, a Small Agricultural Catchment in Southern Sweden

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by

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Abstract

In April 2000, bed sediment cores were collected at three locations in the Vemmenhög area, an intensively farmed catchment in southern Sweden. Additional samples of surface and mobile sediments were collected from April to September at one of the locations. The sediment samples were analysed for 20 pesticides, including 9 herbicides, 3 fungicides and 8 insecticides. The aim of the investigation was to study 1) the occurrence and distribution of mostly currently used pesticides in bed sediment and 2) their temporal variation in surface and mobile sediment during the cropping season. This to examine if these sediments could be used as a 'fingerprint' of historical use as well as reflect current use of pesticides in the area. In addition to this the results were compared with the results of an investigation performed in 1990/91 at the same locations.

Altogether 10 pesticides, including 4 herbicides (diflufenican, diuron, isoproturon and methabenzthiazuron), 2 fungicides (fenpropimorph and propiconazole) and 4 insecticides (DDT, esfenvalerate, permethrin and pirimicarb) were detected. The results show that streambed and pond sediments act as sinks for hydrophobic pesticides in the Vemmenhög area. Six out of twelve pesticides in this investigation having log K_{ow}-values above 3.5 were detected. Of the remaining six pesticides, having log K_{ow}-values above 3.5, five were pesticides which had very limited use in the area during the last decade.

Most of the detected pesticides showed distribution trends in concentration with depth. The results imply that bed sediments in the area has the potential for being used as a historical 'fingerprint' of inputs of pesticides to the freshwater sediment ecosystem. With few exceptions the distribution of pesticide concentrations down through the sediment cores indicate that the input of pesticides to the sediments in the Vemmenhög area are decreasing. To get a more accurate picture, methods of dating relatively young alluvial deposits are needed. Further, it would be valuable to investigate the temporal and spatial variation in sedimentation patterns at the collection sites more thoroughly.

Concentrations of most pesticides detected in surface and mobile sediment showed little temporal variation during the collection period. No elevated amounts of pesticides were found in periods following pesticide application or rain as is common for pesticides detected in surface water in the area. The lack of any trends for most of the detected pesticides is likely an effect of their strong sorption and slow movement in soil in addition with a small or insignificant contribution of pesticides from spills, spray drift and surface runoff, during the investigation period.

Table of contents

4. Materials and methods

5. Results and discussion

1. Introduction

Although the use of pesticides in agriculture has resulted in increased crop production and other benefits, it has raised concerns about potential adverse effects on the environment and the human health. In many respects, the greatest potential for unintended adverse effects of pesticides is through contamination of the hydrological system. In attempting to predict the behaviour of pesticides in surface waters, it is essential to consider the potential partitioning to sediment. Extensive research on this topic has been conducted in many countries and a large number of pesticides have been detected in freshwater sediments during the last decades. Most studies, however, have focused on chlorinated insecticides. Less attention has been directed towards many of the currently used pesticides. In the United States for example over 400 scientific studies have looked for pesticides in stream sediments or aquatic biota during the last 30 years. Ninety-seven percent focused on organochlorine insecticides (USGS 2000). The objective of this investigation was to study the occurrence of currently used pesticides in stream and pond sediment of the Vemmenhög area, a small, well studied, agricultural catchment in southern Sweden (Kreuger 2000). The distribution of pesticides down through the sediment cores and the changes of pesticide concentrations in surface and mobile sediment during the cropping season were investigated to examine if these sediments could be used as a 'fingerprint' of historical as well as current use of pesticides in the area. In addition to this, the results were compared with the results of an investigation performed at the same locations 10 years earlier, in 1990/91.

2. Pesticide sorption - *Its mechanisms and influence on transport*

The sorptive capacity of a certain pesticide will affect its transport and fate in soil as well as in freshwater ecosystems. The most common way of pesticide transport in soil is through movement with water (Torstensson 1987). In this respect, the water solubility and the sorption capacity of the pesticide, as well as the amount of water in movement, are of great importance for the transport velocity of the pesticide. The transport of pesticides sorbed to particles is generally slow. Minute amounts of pesticides associated with particles penetrating cracks and channels in the soil may, however, rapidly reach deep into the soil (Torstensson 1987). Transport of pesticides on the soil surface may either be wind or water mediated. In both cases the sorption capacity of the pesticide is of importance. If sorption is low this will decrease the risk of surface transport due to faster transport down in the soil. If sorption is high a large amount of the applied pesticide will instead stay at the soil surface sorbed to soil particles, which can be moved by wind and surface runoff (Torstensson 1987).

The transport of a pesticide in surface waters depends on the form in which it exists. Pesticides that are associated to particulate matter within the size of sands and clays (2 mm - 0.2 µm) tend to settle out in lakes and reservoirs and in low energy sections of streams. This while transport of dissolved pesticides and pesticides associated with colloidal size particles (0.2 µm - 0.001 µm) are mainly governed by the movement of the water flow (Larson et al. 1997). Particles that once have been settled may be deposited for shorter or longer times. They may resuspend again during high-energy events such as spring runoff and strong wind or they may be buried by bioturbation or new settling sediment.

The sorption of pesticides to particulate matter is a complex process. It is both affected by the physical-chemical characteristics of the pesticide, the characteristics of the particles, and the surrounding solution. Sorption of pesticides may either occur trough adsorption to clay particles, organic material, aluminium and iron oxides or trough chemical interactions with humic substances. Adsorption is a reversible process. A certain amount of the pesticide dissolved in the surrounding solution (pore or stream water) is balanced by a certain amount of pesticide adsorbed to particulate matter (Torstensson 1987). Changes of dissolved pesticide concentration in pore or stream water will thus affect the amount of pesticides sorbed to particulate material. The adsorption or desorption of pesticides is not instantaneous though but may go on for shorter or longer periods. The desorption is generally slower than the adsorption process (Torstensson 1987). In a certain environment the proportions of dissolved pesticide to pesticide adsorbed are determined by the hydrofobicity of the pesticide, which can be quantified to some extent by its water solubility and octanol-water partition coefficient (K_{ow}). Because sorption is a surface process, the characteristics of the particles that have the greatest influence on the extent of sorption is surface area and surface coverage of organic films (Larson et al. 1997). The presence of inorganic salts such as fertilisers, pH, dissolved organic carbon (DOC) and temperature also affect the adsorption process (Torstensson 1987).

3. Literature review

The following is a literature review of studies investigating freshwater sediments for at least some of the currently used pesticides. Studies that only concern organochlorine insecticides have not been considered.

In an investigation of rural ponds in Ontario, Canada, suspected to be contaminated by pesticides, Frank et al. (1990) found 63% of the ponds to have contaminated water. In several ponds also the sediment was analysed and found to contain residues many times higher in concentration than the water. Contamination of the ponds was mainly attributed to be a result of surface runoff, following storm events, and airborne spray drift. Accidental spills also resulted in high pesticide concentrations in some of the ponds.

In the early nineties, House et al. (1992), accomplished a pilot study in the river Windrush catchment, GB. The main objective was to measure the distribution of selected pesticides between water, bed sediment and suspended sediment at three locations in the river. Triazines, having log K_{ow}-values ranging from 2.1-3.1, were found in all the waters but not in the sediments, while parathion, which has a log K_{ow} of 3.83, was detected in all the sediments but not in water samples. Concentrations in suspended sediments were much higher than in bed sediments.

In two separate investigations in Greece, Albanis et al. (1994, 1995) studied the transport of selected herbicides and organochlorine insecticides in five rivers draining agricultural areas. Concentrations of herbicides in sediments were shown to maximise at the time of application, and the concentrations reflected those found in water samples. This while organochlorine compounds were almost at the same level throughout the sampling period. Several herbicides, such as the phenoxy acids, were detected in water but not in sediment samples.

Knight and Cooper (1996) studied insecticide and metal contamination of a mixed cover agricultural watershed in the Otoucalofa Creek, northern Mississippi, USA. Detectable concentrations of currently used insecticides were found in sediment and in water sampled during late summer storm flows, but not in soils or water at normal flow. Water sampled during storms also had elevated levels of suspended solids which indicated that metals and pesticides were transported sorbed on or concurrently with suspended particles during storm flow conditions. Both persistent and currently used pesticides were transient contaminants in water from agricultural fields. The probable mechanism for pesticide transport was in suspended sediment-laden runoff from cultivated fields during storm events. The heterogeneity of pesticide concentrations and distribution patterns in Otoucalofa Creek watershed indicated that hydrophobic contaminants may move from soils to sediments and finally bioaccumulate in fish. Levels of DDT were ten times higher in fish than in sediments and nearly fifty times higher than in soil while concentrations of DDE in fish were more than fifty times higher than the concentrations in sediments and over hundred times the concentration in soil. Fish also had significantly higher levels of endrin, heptachlor epoxide, heptachlor and lindane. Some currently used pesticides, such as methyl parathion and permethrin, were also found at higher levels in fish than in soil, sediment or water, but at much lower concentrations.

Miles and Pfeuffer (1997) investigated the occurrence of pesticides in canals of South Florida. Surface water samples were collected 4-6 times annually and bed sediment samples (upper 10 cm) semi-annually. Samples were analysed for approximately 70 pesticides and degradation products including many currently used pesticides. Many of the pesticides most frequently detected in water samples were used in large amounts in the area. Among the more frequently found pesticides in sediments were pesticides that bind strongly to soil, pesticides that are highly persistent and/or are used in large amounts. In several cases sediments contained higher pesticide concentrations than those found in water.

In 1997 and 1998 Kronvang et al. (2001) investigated bed sediment in 30 Danish streams. The sediments were analysed for 19 physio-chemically different and, except for DDT, currently used pesticides. Sixteen different pesticides were found. The detection frequencies were significantly related to pesticide application in Danish agriculture. Moreover, a significant relationship was established between the number of pesticides detected in each stream and a number of catchment specific properties such as catchment size, land use, soil type and hydrological regime. The study also documented high inter-annual variations in the occurrence of pesticides in streambed sediment. If this is attributable to inter-annual differences in the delivery of pesticides to the streams and/or linked to the processes governing sediment deposition and resuspension in streams remains to be clarified.

Long et al. (1998) studied 'micro-organic' compounds associated with sediments in the Humber rivers in NE England. Thirty compounds were targeted including a range of pesticide groups, e.g. triazines, organophosphorous compounds and synthetic pyrethroids, along with other contaminants. Samples of 'whole-water' (unfiltered water samples including suspended sediment), suspended and bed sediment were collected at six sites including urban, industrial and agricultural areas. Commonly used herbicides, such as atrazine and propazine were detected regularly within sediment samples along with a number of industrial contaminants and synthetic pyrethroid insecticides. The overall occurrence of sediment associated contaminants within these rivers broadly reflected the general differences in land-use. The concentrations of contaminants associated with bed as well as suspended sediment showed no correlation with concentrations measured in the dissolved phase. Differences in contaminant distribution between matrices were found for a number of substances, potentially reflecting the physio-chemical nature of the contaminants. The authors also found considerable temporal and spatial variation within and between rivers in the concentrations of pesticides associated with sediments. It was suggested that these variations reflect a number of factors such as differences in land-use and the effect of seasonal application of contaminants in addition to differences in the sediment characteristics. The concentration of contaminants in suspended sediments generally exceeded that seen in bed sediment. The apparent preference of contaminants for suspended sediments possibly reflected the larger surface-area of suspended material and thus a larger area exposed for sorption.

There is little information available on the distribution of pesticides in freshwater sediments with depth. In 1996 Daniels et al. (2000) collected bed sediment cores in one rural and one dominantly urban river in southern England. Bed sediment cores were collected up to a depth of 1 m. The cores were sectioned in approximately 10 cm intervals and analysed for 'micro-organic' contaminants as well as sediment characteristics. Among the contaminants found were the pesticides carbaryl, linuron, fenpropimorph, the synthetic pyrethroids and prometryn. Although no significant sediment mixing occurred between the river alluvium and the underlying beds, the majority of identified organic contaminants were present in the underlying beds in similar concentrations to those found in the alluvium at both sites. Despite wide variation in distribution of contaminants with sediment depth and position across the channels some generalisations could be made. The more hydrophobic compounds were concentrated up to 400-fold at the top of the cores, relative to concentrations further down. The less hydrophobic compounds had irregular distribution throughout the cores, probably as a result of their translocation in porewaters. The sediment characteristics investigated, including content and composition of clay, surface area, cation exchange capacity (CEC), total and dissolved organic carbon (TOC and DOC respectively) showed little variability within each sediment type and produced poor correlations with contaminant concentrations. The authors concluded that TOC and DOC levels probably were too low to exert a strong influence on contaminant mobility.

4. Materials and methods

4.1 Description of study area

The Vemmenhög catchment is situated in the very south of Sweden, a couple of kilometres south-west of Skurup. The area, 9 km^2 in size, forms the upper reach of the Vemmenhög Stream drainage basin, which empties into the Baltic Sea. It has an undulating topography with an average altitude of 45 meters above sea level, varying from 30 to 65 meters. The catchment is characterised by glacial till-derived soils rich in lime- and flintstone showing that the area is part of the Baltic moraine (Svensson 1999). The topsoil consists mainly of sandy loams with a clay content of 15-20% by weight. The underlying soil is more varied ranging from organic soils to pure sands and clays. The area is, however, as a whole relatively homogenous considering soil texture and other soil physical characters (Svensson 1999). The soil chemistry is more varied but with generally high concentrations of potassium and phosphorus in the top soil, an effect of fertilising and root uptake from deeper soil layers (Svensson 1999). The pH is rather high by Swedish standards due to high calcium oxide content, with a pH of 7.2 (median) in the topsoil, which increases with depth to 7.7 at 75-100 cm (Svensson 1999). The pH value of drainage and stream water is within the range of 7.5-8.0 (Kreuger 1998).

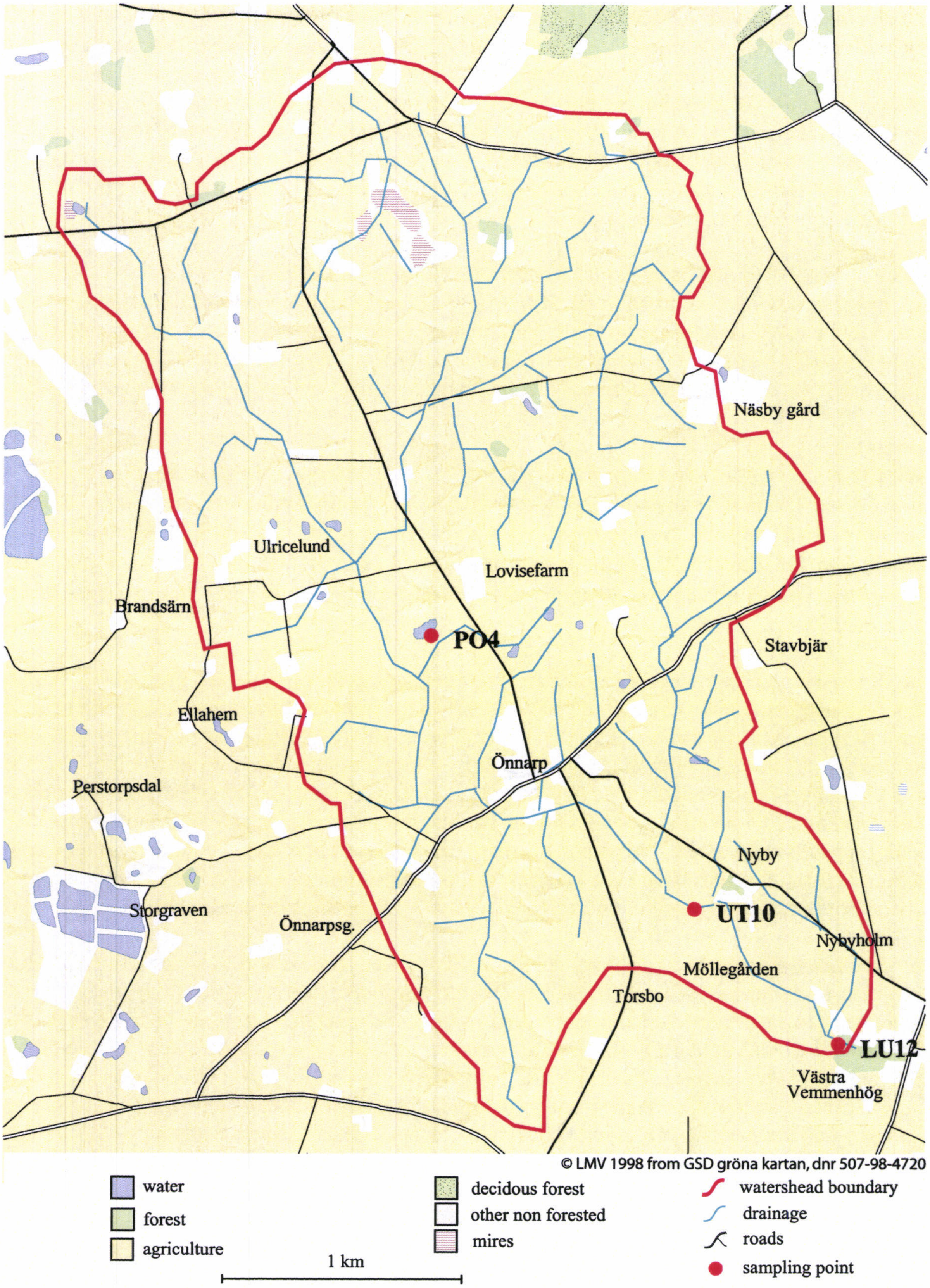

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Figure 1. Land use and location of sampling sites in the Vemmenhög catchment

The area is intensively farmed, 95% of the catchment consist of arable land (Figure 1). To improve the agricultural conditions, extensive drainage systems have been installed within the area. In the 1950's open ditches, as well as the Vemmenhög stream, were covered and replaced by a culvert system (coloured in blue in Figure 1). The water discharges into the open 1.1 km before the catchment outlet. Just north of the outlet the stream has been widened to form a small, 0.2-0.4 meter deep pond. Several smaller ponds are scattered over the area. In the centre of the catchment there is one larger (0.5 ha), 2-5 meter deep pond with the outflow connected to the culvert system, but with no flow trough.

In 1998 a total of 31 farms managed the arable land within the catchment (Kreuger 2000). The non-farming households amounted to about 50. The farming is highly specialised in crop production with a 4-year rotation, normally comprising winter rape, winter wheat, sugar beets and spring barley, on 80% of the cultivated area (Kreuger 1998). Cereal crops dominate the remaining area. The area contains a few pig farms and some horses but the total animal density is very low.

4.2 Climate

The climate in the region is maritime due to the prevailing westerly winds and the vicinity to the Atlantic Ocean. The mean annual temperature is 7.2 °C, with mean summer and winter temperatures of 16 and –1 °C, respectively. The length of the growing season (mean daily temperature >5°C) is around 220 days. The average annual precipitation is 662 mm and falls mainly as rain. Soil temperature at 50 cm depth is 16 °C during summer and drops to around 2 °C during winter (Kreuger 1998).

4.3 Pesticide usage and occurrence in water and sediment

Since 1988 the Vemmenhög catchment has been part of the Swedish environmental monitoring program "Typområden på jordbruksmark" (Kyllmar et al. 2000). The objective of this program is to monitor the influence of agriculture on the quality of surface and ground water within a number of small catchments dominated by arable land in Sweden. Transport of pesticides from the Vemmenhög catchment has been studied as part of this program since 1990. Information on pesticide use within the area has been collected annually through interviews with the farmers, and the occurrence of pesticides have been determined in water samples from the stream. The results have been presented on several occasions (Kreuger 1998, 2000, Kreuger & Hessel 1998).

About 1300-1400 kg of pesticide active ingredients have been applied within the catchment each cropping season (Kreuger 1998). The usage is to a large extent concentrated to spring/early summer (April to early July) when on an average 75% of the total amount of active ingredient is applied on 80% of the catchment area. The usage is largest in May and dominated by herbicide applications (81% by weight) followed by fungicides (15% by weight) and insecticides (3% by weight). The area treated with fungicides and insecticides varies considerably from year to year depending on different weather conditions and occurrence of pests. Certain years only 25% of the total area is treated, but during other years up to 60% of the total area is treated with fungicides and insecticides. Sugar beet, grown on approximately 20% of the area, is the most intensively treated crop, receiving almost half of the total amounts during spring/early summer. Autumn applications are totally dominated by herbicides (99% by weight). Approximately 30% of the catchment area is treated, the amounts corresponding to about 25% of the total usage (Kreuger 1998).

In 1990 the non-farming households were also interviewed concerning pesticide usage. However, less than 10% of the households used pesticides, and these were mainly herbicides in small amounts (Kreuger 1998).

A total of 38 pesticides including 30 herbicides, four fungicides, three insecticides and one metabolite of one of the herbicides has been detected in water samples from the Vemmenhög area (Kreuger 1998). Stepwise multiple regression analysis to express concentration, transported amount and loss rate as functions of different pesticide intrinsic properties and quantities applied was conducted using monitoring data of 25 pesticides during 1990-1994 (Kreuger and Törnqvist 1998). The single most significant variable was quantities applied, accounting for 50-85% of the variability in concentration and transport losses during individual years. Evaluation of loss rate, in percent of applied quantities, using simple linear regression analysis identified log K_{ow} as the most significant variable for pesticide loss to surface water (Kreuger and Törnqvist 1998).

In 1990/91 stream and pond sediment samples were collected within the Vemmenhög catchment area and analysed for a wide range of persistent and currently used pesticides (Kreuger et al. 1999). Eleven pesticides were detected, with fungicides and insecticides being those most commonly found. The investigation demonstrated the importance of pesticide distribution between matrices. Many of the pesticides detected in sediment samples in highest concentrations were either not detected or only detected in low amounts in water samples from the area. Six out of nine pesticides having a log K_{OW}-value higher than 3.5 were detected in the sediment samples despite having quite limited or no use at all during the investigation period.

The current investigation was to some extent a repeat of those performed in 1990/91. Three out of four sampling sites used in 1990/91 were utilised again, but instead of collecting unsectioned bed sediment cores the cores in the current investigation were sectioned before analysis. Further, mobile sediments were collected during a longer period and, additionally, surface sediments were collected for comparison.

4.4 Site locations and sample collection

Bed sediment cores were collected on April 11-12, 2000, from I) the larger pond in the middle of the catchment at site PO4 (Figure 1), II) from the open stream a few hundred meters after the culvert outlet at site UT10 (just were the stream bends) and III) from the small pond just before the catchment outlet at LU12. At LU12 and PO4 a small boat was used during the sampling procedure. The cores were collected using a coring device made of stainless steel and acrylic plastic tubing, 60 cm in length and 7.5 cm o.d. and 7.0 cm i.d., reinforced with a sharp edge of stainless steel at the bottom. To facilitate the sampling procedure the coring device was equipped with a frame with 3.0 kg of weights. At the top end of the corer a vertically movable lid allowed air to vent during coring insertion, and during core extraction maintained a vacuum, by tight closure, thus holding the sediment in place. At each location, four different subsamples were collected. Cores from LU12 and PO4 were split into four different sections using an acetone-rinsed knife: 1) surface sediment (fluid, more or less suspended sediment), and 2) 0-2.5 cm, 3) 2.5-10 cm and 4) 10-12.5 cm. The bed sediment in the narrow part of the Vemmenhög stream at UT10 was not as thick as at the two other locations and the higher water velocities prevent the formation of a fluid surface layer. Therefore, sediment cores to a depth of only 7.5 cm were collected which was split into two different sections: 1) 0-2.5 cm and 2) 2.5-7.5 cm.

Additional surface sediment was collected at LU12 with monthly intervals from mid May to mid September. Mobile sediments were collected on five occasions from sediment traps located in the stream closely after the small pond at LU12. The sediment was trapped in acetone-rinsed glass jars placed in the bottom sediment with the opening a few centimetres over the surface. The collection periods, each of approximately one month in length, started on April 12, May 11, June 13, July 10 and August 14 respectively.

After collection all sediments were transferred to acetone-rinsed glass jars which were put two and two in styrofoam boxes with ice, and were returned to the laboratory within 48 hours and stored at -18°C prior to analysis.

4.5 Water flow

Water flow at the culvert outlet at UT10 was measured continuously during the investigation period, using a 90-degree V-notch weir and an ultrasonic sensor (ISCO model 3210 flowmeter with a plotter).

4.6 Chemicals

All organic solvents were obtained from Lab-Scan Analytical Science, Dublin, Ireland, and were of pesticide grade. Hydromatrix (Varian Sample Preparation Products, Harbor City, CA, USA) and sodium sulphate (Merck, Darmstadt, Germany), heated to 550 C >8 h and stored in a desiccator, were used as drying agents. Concentrated sulphuric acid was also obtained from Merck, Darmstadt, Germany.

Internal standard solutions, hexabromobenzene (HBB) (4.144 μg/ml) and etion, (1.664 μg/ml) were prepared in cyclohexane and acetone, respectively, from pure compounds (etion 95% purity and HBB 98% purity) provided by Dr Ehrenstorfer GmbH, Augsburg, Germany.

External standard solutions, ranging in concentration from 0.004-0.81 μg/ml, and standard solutions used in the recovery tests with concentrations ranging from 0.2-10 μg/ml, were prepared in cyclohexane/acetone 9:1 (v/v) from stock solutions or pure compounds (98-100% purity), all provided by Dr Ehrenstorfer GmbH, Augsburg, Germany.

4.7 Extraction procedure and chemical analysis

A total of 20 pesticides including 9 herbicides, 3 fungicides and 8 insecticides were determined (Table 1). The pesticides determined were chosen considering their hydrophobicity and persistence, their present and historical use in the area, and earlier findings of pesticides in sediments in the area. Findings of pesticides in the studies reviewed were also considered.

The pesticide residues in the sediments were determined using methods developed at the Organic Environmental Chemistry Unit, Department of Environmental Assessment at the Swedish University of Agricultural Sciences in Uppsala, Sweden, through modification of methods originally developed for analysis of water and described by Åkerblom et al. (1990).

Excess water was carefully removed and the subsamples from each collection site were thoroughly mixed. Sediment dry weight was determined after heating at 105°C for 16 hours, using duplicate samples of each sediment. Twenty grams of wet sediment from each sample were ground with Hydromatrix as a drying agent (0.5 to 0.75 g/g wet sediment depending on water content). After grinding, mixtures corresponding to 6 g of wet sediment were extracted with

Table 1. Pesticides determined and total amounts applied in the Vemmenhög catchment during the period 1990-1998. Information of pesticide type and values of different compound properties measured at 20-25 °C are also given

Substance[a]	**Type**	**Selected trade names**[b]	**Amount**[c] (kg)	**log K_{ow}**[d]	**Solubility**[e] (mg/l)	**DT_{50}**[f] (days)
aclonifen	Herbicide	Fenix	7.3 (96-)	4.4	1.4	36-80
alfa-cypermethrin	Insecticide	Fastac	0.1 (90)	6.9	0.01	~91
atrazine (1989)	Herbicide	Totex strö	0.2 (90) + f.y.[g]	2.5	33	16-77
cyfluthrin	Insecticide	Baytroid 050 EC	3.12 (90-)	5.9-6.0	0.002	116
DDT (1970)	Insecticide	n.i.[g]	n.u.[g]	6.2	0.006	2000
deltamethrin	Insecticide	Decis	2.91 (90-)	4.6	<0.0002	~23
diflufenican	Herbicide	Cougar	63.5 (93-)	4.9	<0.05	100-200
diuron (1992)	Herbicide	Karmex 80	n.u.	2.9	36.4	90-180
esfenvalerate	Insecticide	Sumi-alpha 5 FW	26.8 (90-)	6.2	0.002	71-287
ethofumesate	Herbicide	Partner, Tramat 50 CS	258.6 (90-)	2.7	50	84-407
fenpropimorph	Fungicide	Tilt Top 500 EC	845.2 (90-)	4.1	4	15-93
isoproturon	Herbicide	Arelon Flytande, Cougar,Tolkan	948.8 (90-)	2.5	65	6-28
lambda-cyhalohtrin	Insecticide	Karate 2.5 EW	5.5 (94-)	7.0	0.005	28-84
metazachlor	Herbicide	Butisan S	845.5 (90-)	2.1	430	~77
methabenzthiazuron	Herbicide	Tribunil	231.1(-97)	2.6	64	135
permethrin	Insecticide	Talcord	n.u.	6.1	0.2	~38
pirimicarb	Insecticide	Pirimor	175.5 (90-)	1.7	3000	7-234
prochloraz	Fungicide	Sportak	67.7 (-93)	4.1	34.4	5-37
propiconazole	Fungicide	Tilt Top 500 EC	250.0 (90-)	3.7	100	40-70
terbuthylazine	Herbicide	Topogard 500 FW,Gardoprim	7.3 (93-) + f.y.	3.2	8.5	30-60

[a] Substances in italic are withdrawn from the Swedish market. Year of withdrawal is shown in brackets

[b] Information on trade names from the National Chemicals Inspectorate, Sweden, (www.kemi.se)

[c] Information on usage from Kreuger (1996, 1997, 1998, 2000). Year when application started and/or ended is shown in brackets. (90–) announce that the pesticide has been used the entire period between 1990 and 1998

[d] Values for octanol-water partition coefficient from Tomlin (1998)

[e] Values for water solubility from Tomlin (1998)

[f] Values for half-life in soil from Tomlin (1998). Values for average half-life in soil for cyfluthrin and methabenzthiazuron from Linders et al. (1994), for DDT from Mackay et al. (1997)

[g] f.y.= farmyard application, no information on amounts used; n.i.= no information; n.u.= not used

acetone/dichloromethane, 1:1 (v/v) at 170°C using a Soxtec Avanti model 2050 Auto extraction system (FOSS Tecator, Höganäs, Sweden). Hexabromobenzene (HBB) and etion in amounts corresponding to 0.02 and 0.06 µg/g wet sediment, respectively, were added to the extraction thimble before extraction as internal standards. Each sample was extracted for two hours submerged in the solvent and one hour in the rinsing position. Blank extracts were prepared following the procedure for the sediment analysis but without any sediment in the extraction thimble. Extracts were dried by addition of sodium sulphate, filtered, evaporated and the volume was finally adjusted to 2 ml with cyklohexane/dichloromethane, 1:1 (v/v). One ml of each extract was cleaned by gel permeation chromatography (GPC) and the volume of the eluate adjusted to 1 ml with cyclohexane/acetone, 9:1 (v/v), before final determination, using GC-MS (gas chromatography-mass spectrometry). For analysis of DDT, DDD and DDE half of the cleaned extracts were further purified with sulphuric acid after removal of acetone and adjustion of the volume to 1 ml with pure cyclohexane. GC-EC (gas chromatography with electron capture detection) was used for the final determination of these compounds.

4.8 GC-EC and -MS conditions

The GC-EC had dual detectors and was operated with splitless injection (injection volume 2 µl), using fused silica columns, CP-SIL 5 CB and a CP-SIL 19 CB with dimensions 30 m x 0.32 mm i.d. and 0.25 µm film thickness, provided by Chrompack Sverige AB, Nacka, Sweden. Nitrogen served as carrier gas. The injection temperature was 250°C. The oven was set to 90°C for 1 min, thereafter increasing with 30°C/min to 180°C and then with 4°C/min to 260°C where it was held for 12 min. The GC-EC interface temperature was set to 300°C. A chromatograph data system, Chromeleon (Gynkotek HPLC, Germening, Munich, Germany), was used for collection of chromatographic data.

The GC-MS was operated with splitless injection (injection volume 2 µl). The gas chromatograph (Hewlett Packard, model 5890) was equipped with a fused silica column, CP-SIL 5 CB (60 x 0.25 mm i.d. and 0.25 µm film thickness) provided by Chrompack Sverige AB, Nacka, Sweden. The injector temperature was 250°C. The oven was set to 90°C for 1 minute, thereafter increasing with 30°C/min to 210°C and then with 4°C/min to 290°C where it was held for 16 minutes. Helium served as carrier gas. Attached to the gas chromatograph was a mass spectrometer (VG Instruments, model TRIO 1). The GC-MS interface temperature was 290°C. The mass spectrometer was operated in the electron ionisation (EI) mode at 70 eV electron energy, or in the negative ion chemical ionisation (NCI) mode. Methane served as reactant gas for determination with NCI. Data were collected using selected ion monitoring (SIM) with three characteristic ions per compound.

Quantification with both GC-MS and GC-EC was performed by internal and external standard calibration based on the height of the chromatographic peaks.

4.9 Pesticide recovery tests

Recovery tests for the pesticides included in the investigation were performed at two occasions using surface sediment collected at PO4 in April 2000. At both occasions three samples, each of 20 g of wet sediment, were mixed with pesticides in known amounts (Table 2). Each sample was mixed with one out of three different standard solutions containing pesticides for determination with GC-EC or GC-MS with EI or NCI respectively (Table 2). A fourth sample of 20 g of wet sediment was used as a blank. After mixing the sediment samples with the standard solutions the

Table 2. Method for determination, added amount of pesticide to the sediment collected at PO4 in April 2000, recovered amount and % recovery, determined at two separate occasions

pesticide	method for determination[a]	recovery test	added amount (µg/g dw)	recovered amount (µg/g dw)	recovery (%)	mean recovery (%)
aclonifen	NCI	1	0.170	0.067	39	
		2	0.145	0.052	36	38
alfa-cypermethrin	NCI	1	0.045	0.033	73	
		2	0.038	0.030	79	76
atrazine	EI	1	0.049	0.056	115	
		2	0.042	0.040	95	105
cyfluthrin	NCI	1	0.086	0.064	75	
		2	0.074	0.059	80	77
DDT-p,p	EC	1	0.045	0.036	80	
		2	0.045	0.029	64	72
DDT-o,p	EC	1	0.045	0.040	89	
		2	0.045	0.032	71	80
DDE -p,p	EC	1	0.034	0.036	105	
		2	0.034	0.029	86	96
DDD -p,p	EC	1	0.023	0.018	79	
		2	0.023	0.014	64	72
deltamethrin	NCI	1	0.361	0.275	76	
		2	0.309	0.223	72	74
diflufenican	NCI	1	0.170	0.132	78	
		2	0.145	0.090	62	70
diuron	EI	1	0.069	0.195	281	
		2	0.059	0.056	95	188
esfenvalerate	EI	1	0.037	0.027	74	
		2	0.032	0.027	84	79
ethofumesate	EI	1	0.147	0.310	210	
		2	0.125	0.162	129	170
fenpropimorph	EI	1	0.188	0.110	59	
		2	0.160	0.093	58	59
isoproturon	EI	1	0.052	0.169	326	
		2	0.044	0.084	190	258
lambda-cyhalohtrin	NCI	1	0.036	0.031	85	
		2	0.031	0.027	87	86
metazachlor	EI	1	0.237	0.122	51	
		2	0.202	0.109	54	53
methabenzthiazuron	EI	1	0.283	0.420	148	
		2	0.241	0.286	119	134
permethrin	NCI	1	0.104	0.089	86	
		2	0.089	0.079	88	87
pirimicarb	EI	1	0.094	0.162	172	
		2	0.080	0.123	154	163
prochloraz	NCI	1	0.251	0.142	56	
		2	0.215	0.117	54	55
propiconazole	NCI	1	0.088	0.094	107	
		2	0.076	0.117	154	130
terbuthylazine	EI	1	0.052	0.049	95	
		2	0.044	0.037	84	89

[a] NCI = GC-MS operated in the negative ion chemical ionisation mode, EI = GC-MS operated in the electron ionisation mode and EC = GC-EC

samples were allowed to stand for an hour after which all samples were treated following the procedure for the sediment analysis as outlined above.

4.10 TOC

Total organic carbon (TOC) was determined at the Department of Soil Science at the Swedish University of Agricultural Sciences, Uppsala, Sweden . TOC was determined through combustion at 1250°C using a LECO CN 2000 system. The sediments were dried at 40°C for 72 hours, ground through a 2 mm sieve and acidified with 10 M HCl to remove carbonate carbon before analysis.

5. Results and Discussion

5.1 Water flow

The cropping season 2000 was characterised by a dry and early spring which contributed to a considerable decrease of streamflow at UT10 from initial high values in April to the end of May (Figure 2). Water flow continued to decrease until the beginning of September as a consequence of high evapotranspiration and relatively small amounts of rain in July and August.

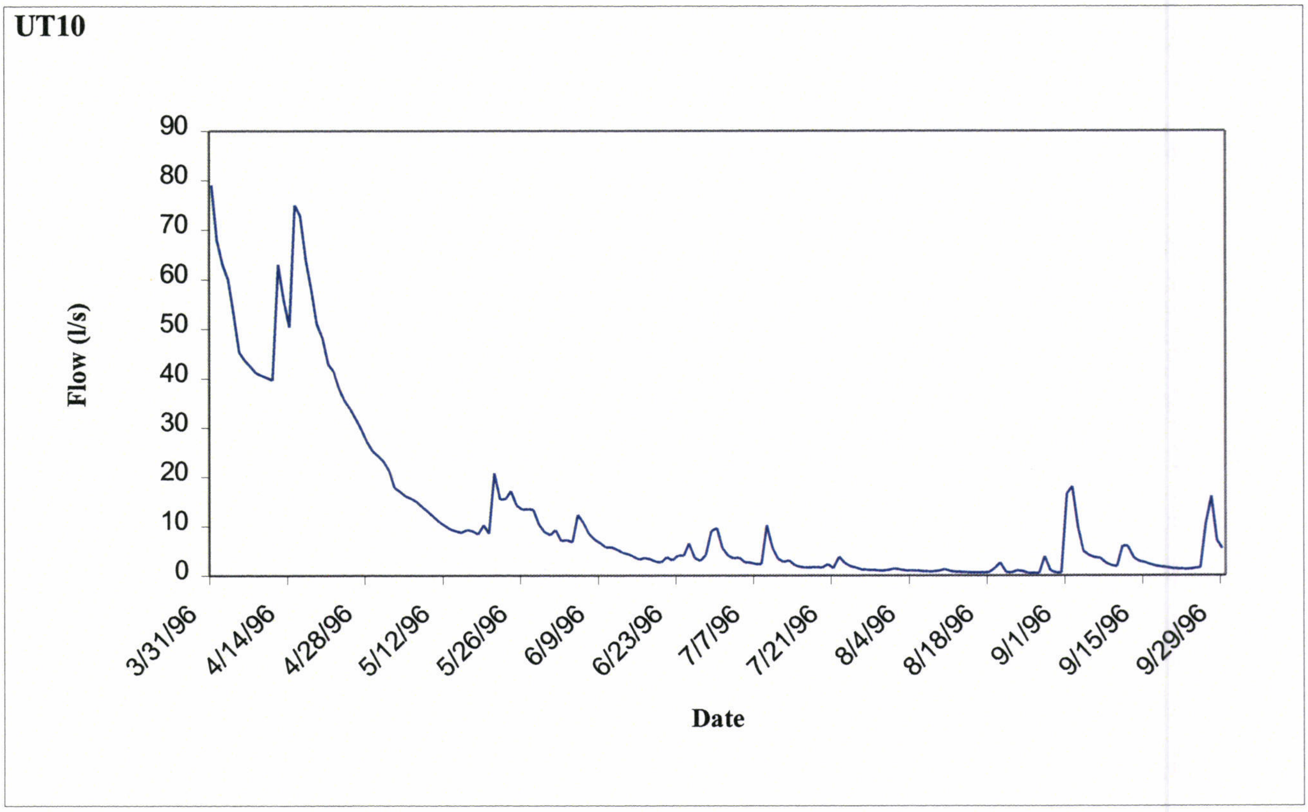

Figure 2. Water flow in the Vemmenhög stream (l/s)

5.2 Recoveries

The mean recoveries for most compounds was within the range of 70-134% (Table 2). Aclonifen 38%, fenpropimorph 59%, metazachlor 53% and prochloraz 55% had a lower mean recovery than the other pesticides while pirimicarb 163% had a higher mean recovery than the other pesticides. The recoveries for isoproturon, diuron and ethofumesate were also high and varied greatly between the two recovery tests as well. Attempts to determine the recoveries associated with the analysis of surface and mobile sediments from LU12 (surface sediment in April not included) gave recovery efficiencies of 326%, 281% and 210% for isoproturon, diuron and ethofumesate, respectively. This while attempts associated with the analysis of sample LU12 Surface, LU12 10-12.5, PO4 2.5-10, PO4 10-12.5, UT10 0-2.5 and UT10 2.5-7.5 gave recovery efficiencies for the same substances of 190%, 95% and 129%, respectively. Unfortunately, recovery efficiencies associated with the analysis of the remaining four samples from LU12 and PO4 are not available. None of the reported results were corrected for recoveries.

5.3 Detection limits

The background noise during pesticide analysis varied considerably between different samples, therefore no general limits of detection for the compounds could be determined. Instead a limit of detection, corresponding to three times the background noise (Table 3 and Table 4), and a limit of determination corresponding to six times the background noise was determined for each compound in every individual sample. The varying background noise between individual samples made evaluation of the results complex for a number of pesticides, such as fenpropimorph, methabenzthiazuron and propiconazole. It is likely that some samples had undetected concentrations of pesticides.

5.4 Pesticides detected

Including total DDT, altogether 10 out of 20 pesticides analyzed for were detected (Table 5-9). Among the pesticides detected were 4 herbicides (diflufenican, diuron, isoproturon and methabenzthiazuron), 2 fungicides (fenpropimorph and propiconazole) and 4 insecticides (DDT, esfenvalerate, permethrin and pirimicarb). At LU12 all 10 pesticides were detected in bed sediment samples, 9 in surface sediment and 7 in mobile sediment. At PO4, 5 pesticides were detected in bed sediment samples, and at UT10, 6 pesticides were detected in bed sediment samples. All pesticides included in the analyses and detected in sediment samples in 1990/91, except for prochloraz, were detected also during the investigation in 2000. Further, isoproturon, analyzed for but not detected in1990/91, was found in bed sediment samples at LU12, PO4 and UT10 as well as in surface and mobile sediment at LU12. Pirimicarb, also analyzed for but not detected in 1990/91, was found in bed sediment samples from LU12 and PO4. Four pesticides not included in 1990/91, aclonifen, alfa-cypermethrin, diflufenican and lambda-cyhalotrin were also included in the investigation in 2000. Of these only diflufenican was found.

The results show that streambed and pond sediments act as sinks for hydrophobic pesticides in the Vemmenhög area. Six out of twelve pesticides in this investigation having log K_{ow}-values above 3.5 were detected. Of the remaining six pesticides, having log K_{ow}-values above 3.5, five were pesticides which had very limited use in the area during the last decade. The exception is prochloraz, a fungicide that was used extensively in the beginning of the 90's. However, the use of prochloraz ceased already in 1993, and the pesticide has despite a relatively high log K_{ow}-value, a solubility in water and a half-life in soil corresponding to the less hydrophobic pesticides.

Table 3. Detection limits (µg/kg dw) for pesticides analysed in bed sediment samples collected in Vemmenhög in April 2000

	Location and depth (cm)									
	LU12				**PO4**				**UT10**	
Pesticide	surface	0-2.5	2.5-10	10-12,5	surface	0-2.5	2.5-10	10-12.5	0-2.5	2.5-7.5
aclonifen	1	1	2	2	1	2	1	2	0.5	1
alpha-cypermethrin	0.5	1	1	1	1	1	2	1	0.5	1
atrazine	8	15	40	60	50	25	3	4	1	5
cyfluthrin	1	1	3	1	4	1	2	2	0.5	1
DDT-p,p	4	4	4	4	4	3	3	3	2	2
DDT-o,p	1	1	1	1	2	2	2	2	1	1
DDE-p,p	1	2	2	2	4	2	3	1	1	1
DDD-p,p	4	4	4	4	3	3	2	1	1	2
deltamethrin	2	2	3	2	3	1	2	2	1	1
diflufenican	2	2	3	2	3	5	5	5	0.5	1
diuron	0.5	1	0.5	0.5	20	15	1	0.5	0.5	0.5
esfenvalerate	1	1	2	2	7	4	2	3	3	2
ethofumesate	9	20	20	4	50	35	1	5	0.5	2
fenpropimorph	3	30	40	30	90	70	1	2	1	10
isoproturon	3	3	3	2	13	25	5	7	0.5	1
lambda-cyhalothrin	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
metazachlor	45	400	800	400	150	150	30	100	20	30
methabenzthiazuron	9	25	350	450	10	10	15	25	10	12
permethrin	2	6	6	6	9	8	9	11	2	2
pirimicarb	15	7	10	6	10	10	3	15	5	8
prochloraz	25	25	60	35	90	40	30	30	20	30
propiconazole 1[a]	6	5	7	8	30	25	10	20	7	14
propiconazole 2[a]	20	60	250	120	9	10	3	15	3	7
terbuthylazine	15	20	35	40	9	9	2	1	1	15

[a] The pesticide consists of two different isomers in equal amounts which had different detection limits

Table 4. Detection limits (µg/kg dw) for pesticides analysed in surface and mobile sediment samples collected from April to September 2000 in the small pond at LU12 in Vemmenhög

	surface sediment						**mobile sediment**				
Pesticide	April	May	June	July	Aug.	Sept.	April-May	May-June	June-July	July-Aug.	Aug-Sept.
aclonifen	1	20	20	20	25	30	20	25	25	25	25
alpha-cypermethrin	0.5	2	2	5	4	6	2	2	2	3	3
atrazine	8	8	9	9	9	13	10	8	10	9	15
cyfluthrin	1	3	2	2	3	6	3	2	2	4	5
DDT-p,p	4	2	4	2	3	3	3	5	7	5	6
DDT-o,p	1	2	3	3	1	3	1	1	3	1	2
DDE-p,p	1	2	2	2	2	2	2	3	3	3	2
DDD-p,p	4	3	3	3	2	3	3	3	3	3	4
deltamethrin	2	15	3	3	15	20	9	5	10	15	20
diflufenican	2	3	3	3	6	6	4	3	3	4	6
diuron	0.5	1	1	1	2	3	1	2	3	3	10
esfenvalerate	1	1	2	1	3	4	1	1	1	2	4
ethofumesate	9	25	35	25	20	25	35	35	30	20	40
fenpropimorph	3	30	9	9	30	30	25	7	30	30	30
isoproturon	3	2	2	2	2	2	2	3	2	2	3
lambda-cyhalothrin	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
metazachlor	45	70	70	110	110	150	20	50	20	40	50
methabenzthiazuron	9	45	45	45	45	45	45	45	45	45	45
permethrin	2	3	2	70	5	11	3	0.5	1	3	8
pirimicarb	15	15	15	15	15	20	30	15	15	15	20
prochloraz	25	45	25	70	70	90	25	15	40	60	100
propiconazole 1[a]	6	8	6	11	10	10	4	6	6	25	50
propiconazole 2[a]	20	45	25	60	40	30	11	10	15	20	20
terbuthylazine	15	15	15	13	14	14	25	13	13	13	25

[a] The pesticide consists of two different isomers in equal amounts which had different detection limits

Three of the remaining four pesticides detected, isproturon, methabenzthiazuron and diuron, were so called urea herbicides. The remaining pesticide was pirimicarb, an insecticide that is applied in relatively large amounts in the Vemmenhög area. The findings of less hydrophobic pesticides in the sediments indicate that the hydrofobicity-related adsorption process is not the only process affecting sorption of pesticides to particulate material. Chemical binding of pesticides to humic material may be important for certain pesticides such as the urea herbicides.

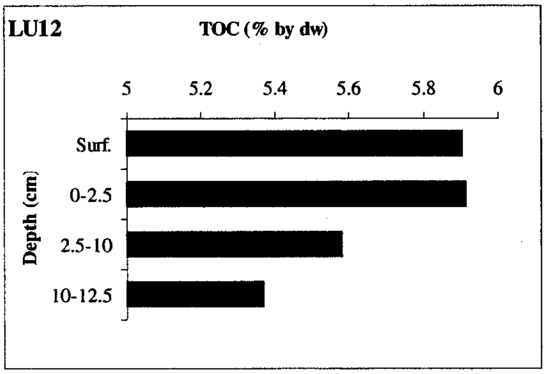

Figure 3. Total organic carbon content (TOC) in bed sediment samples collected in the small pond at LU12 in the Vemmenhög catchment, April 2000

5.4.1 LU12

The bed sediment cores in the pond at LU12 were dominated by clay and showed no visual stratigrafical differences with depth. The uppermost surface sediment, consisting of fluid, suspended, or nearly suspended sediment ranged from 1-2 cm in thickness. The total organic carbon (TOC) content increased slightly from the surface sediment to the 0-2.5 cm section after which it started to decrease with depth, concentrations ranging from 5.4-5.9% by dry weight (Figure 3).

Table 5 . Concentrations (µg/kg dw) of pesticides detected in bed sediment samples collected in the small pond at LU12, together with concentrations of pesticides detected in bed sediment at LU12 in 1991 (Kreuger et. al 1999)

LU12	Year of collection and depth (cm)				
	2000				**1991**
Pesticide	Surface	0-2.5	2.5-10	10-12.5	0-10
DDT-p,p	**25**[a]	<4[a]	<4	<4	**3**
DDT-o,p	<1	<1	<1	<1	n.d.[b]
DDE-p,p	**7**	**7**	**12**	**12**	**5**
DDD-p,p	<4	<4	<4	*6*[a]	**4**
diflufenican	**11**	**12**	*5*	*2*	n.a[b].
diuron	**5**	**7**	**13**	**44**	**2**
esfenvalerate[c]	**5**	**17**	**48**	**36**	**80**
fenpropimorph	**16**	<30	<40	**75**	**200**
isoproturon	**10**	**10**	**8**	**7**	n.d.
methabenzthiazuron	**27**	**71**	<350	<450	n.d.
permethrin	*4*	*8*	**18**	**19**	**3**
pirimicarb	<15	*8*	*11*	*19*	n.d.
propiconazole 1[d]	*7*	**19**	**46**	**27**	**30**
propiconazole 2[d]	<20	<60	<250	<120	

[a] Figures in bold are above the limit of determination (6 times the background noise), figures preceeded by < are method detection limits (3 times the background noise), figures in italic are above the method detection limit but below the limit of determination and therefore only indicative

[b] n.a.= not analyzed; n.d.= not detected

[c] The figure for 1990 refer to fenvalerate

[d] The pesticide consists of two different isomers in equal amounts but only one has been detected.

The pesticides found in highest concentrations at LU12 were methabenzthiazuron and fenpropimorph (Table 5). Methabenzthiazuron is a urea herbicide, which is highly persistent and strongly sorbed in soil (Tomlin 1998). This despite relatively high water solubility and moderate octanol-water coefficient (Table 1). Findings of methabenzthiazuron were located to the two upper sections of the cores with the highest concentration in the 0-2.5 cm section. Possible detection in the deeper sediment was prevented by the high detection limits in these sections. In 1991 methabenzthiazuron was found in mobile sediment at LU12 and in sediment cores at UT10 but not in bed sediment cores at LU12. Possible findings may have been prevented by high limits of detection also this year. Methabenzthiazuron was previously used to control a broad spectrum of broad-leaved weeds and grasses in cereals and pastures, but is since 1999 only allowed for use against certain grass weeds in grass seed pastures (KemI 2001). In 1990-1991 about 10 farms used the herbicide both in spring and in the autumn (J. Kreuger, personal communication). Since then the use of methabenzthiazuron has decreased considerably in the area. In 1993 only one farm used the pesticide and since 1995 the use of methabenzthiazuron has only been reported once.

Diuron and permethrin, two pesticides that have not been used for more than a decade in the Vemmenhög area were also detected in bed sediments at LU12. The highest concentrations were found at the bottom of the sediment cores in the 10-12.5 cm section (Table 5). Concentrations decreased substantially closer to the sediment/water interface. For diflufenican, a herbicide applied for the first time in the Vemmenhög area in 1993, the situation was reversed. The concentrations were highest in the uppermost sections, decreasing with depth. In water samples from the Vemmenhög area permethrin has only been detected once before, in June 1990 (Kreuger 1996). Diuron has been detected more frequently but mainly in low concentrations. The last time diuron was detected in water from the Vemmenhög area was in November 1997 (Kreuger 1997, 2000, Kreuger and Hessel 1998).

The most frequently found pesticides in 1990/91 were the fungicides fenpropimorph and propiconazole, and the insecticide fenvalerate. Fenvalerate was withdrawn from the Swedish market in 1990 (KemI 2001), and substituted by its close relative esfenvalerate, (consisting of the isolated, active isomer). Fenpropimorph, propiconazole and esfenvalerate were all found in bed sediment cores at LU12 in April 2000 (Table 5). All three pesticides, similarly to diuron and permethrin, exhibited trends with increasing concentrations down the core at LU12. Though, for esfenvalerate and propiconazole the concentrations were highest in the 2.5-10 cm section. Concentrations of esfenvalerate and fenpropimorph down trough the cores collected in 2000 were considerably lower than the concentrations found in bed sediment cores in 1991. The highest concentrations detected in 2000 corresponded to half or less than half of the concentrations found in 1991. Concentrations of propiconazole were of about the same magnitude on both occasions.

It might have been expected that the sediments in the shallow pond at LU12 would be thoroughly mixed by bioturbation and alternating sedimentation and resuspension events. The clear concentration gradients for many of the detected pesticides down through the core imply that this is not the case, at least not in the deeper sections. The situation in the surface sediment, though, is unclear. Mixing of the uppermost layers may occur under certain conditions, such as storm events. Transport of the more water soluble pesticides in pore water within the cores may add further confusion to any historical record of deposition in the sediments, in accordance with the suggestion by Daniels et al. (2000). At LU12 the only pesticide showing less variation with depth is isoproturon. This could be the result of redistribution within the sediment. Except for pirimicarb, isoproturon was the pesticide having the lowest octanol-water partitioning coefficient of all detected pesticides. However, the lack of a gradient may also be a result of similar inputs of isoproturon to the sediment during the past years.

Concentrations of most pesticides are lowest near the surface, which imply that input of pesticides to the sediments is decreasing. A decrease of pesticide concentrations in water from the Vemmenhög stream has earlier been reported by Kreuger (1998). This decrease is partly due to measures taken to increase the awareness of the farmers to minimise contamination from spillage and other point sources. The decrease in pesticide concentrations is probably also a result of generally better management practices, a slight changeover to substances that is active at lower dosage, a slight decrease in the number of farmers handling and applying pesticides in the area and increased usage of glyphosate, a herbicide which could not be included in the analyses.

5.4.2 UT10

The bed sediment cores at UT10 showed clear stratigrafical differences with depth. The uppermost 2.5 cm consisted mainly of sand and gravel, while clay and silt dominated the 2.5-7.5 cm section. The total organic carbon content varied greatly with depth being only 0.4% by dry weight in the 0-2.5 cm section, increasing with depth to 1.9% by dry weight in the 2.5-7.5 cm section (Figure 4).

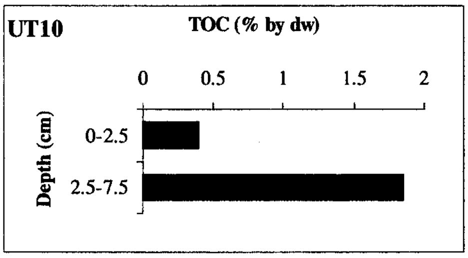

Figure 4. Total organic carbon content (TOC) in bed sediment samples collected in the stream at UT10 in the Vemmenhög catcment, April 2000

Table 6. Concentrations (µg/kg dw) of pesticides detected in Bed sediment samples collected in the stream at UT10, together with concentrations of pesticides detected in bed sediment at UT10 in 1991 (Kreuger et. al 1999)

UT10	Year and depth (cm)		
	2000		**1991**
Pesticide	0-2.5	2.5-7.5	0-10
DDT-p,p	<2[a]	<2	**1**[a]
DDT-o,p	<1	<1	n.d.[b]
DDE-p,p	<1	**2**	**2**
DDD-p,p	<1	<2	**1**
diflufenican	**2**	**7**	n.a[b].
diuron	**1**	**4**	*1*
esfenvalerate[c]	<3	*3*[a]	**30**
fenpropimorph	*2*	<10	**20**
isoproturon	**2**	**2**	n.d.
methabenzthiazuron	<10	*16*	**30**
permethrin	<2	<2	*1*
prochloraz	<20	<30	**60**
propiconazole 1[d]	<7	<14	**20**
propiconazole 2[d]	<3	<7	

[a] Figures in bold are above the limit of determination (6 times the background noise), figures preceded by < are method detection limits (corresponding to 3 times the background noise), figures in italic are above the method detection limit but below the limit of determination and therefore only indicative

[b] n.a. = not analyzed; n.d.= not detected

[c] The figure for 1990 refer to fenvalerate

[d] The pesticide consists of two different isomers in equal amounts which had different detection limits

The higher water velocities at UT10 results in deposition of coarser grained alluvial material with lower surface area than the sediments at LU12 and thus less pesticide adsorption and binding sites. The deposition of finer grained particulate matter is restricted to periods of low flow. This is also periods when the leakage of pesticides down through the soil profiles to the drainage system is brought to a minimum. Pesticide concentrations at UT10 were generally lower than at LU12 (Table 6). In several cases pesticides detected in the pond at LU12 were not detected at UT10 at all (permethrin, pirimicarb, propiconazole).

The concentration gradients down through the sediment cores at UT10 are to a large extent influenced by the differences in sediment composition. All pesticides except isoproturon showed their highest concentration in the 2.5-7.5 cm section at UT10. This includes diflufenican, which had the highest concentrations in surface sediment at LU12. Pesticide concentrations at UT10 in 2000 were all considerably lower than in 1991. This is probably due to a combination of factors including a decrease in pesticide input to the Vemmenhög stream, and the time of sediment collection in relation to sedimentation patterns and pesticide application peaks in the area.

5.4.3 PO4

The fluid surface section in bed sediment cores at PO4 varied in thickness from approximately five to fifteen centimeters. The cores were dominated by clay and had a high TOC content

(Figure 5), probably as a consequence of slow water turnover and anoxic conditions at the bottom of the pond. The TOC content decreased with depth from 16.2% by dry weight to 13.2% by dry weight in the 10-12.5 cm section.

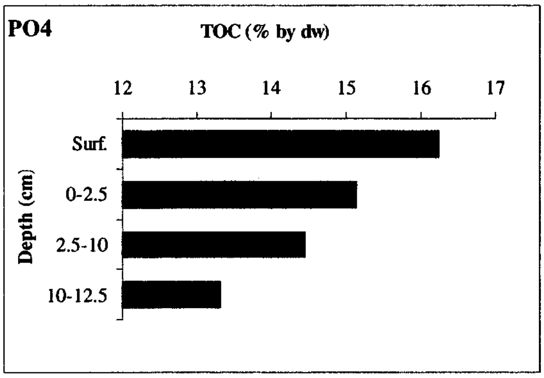

Figure 5. Total organic carbon content (TOC) in bed sediment samples collected in the stream at UT10 in the Vemmenhög catcment, April 2000

The pesticide found in highest concentration at PO4, as well as at LU12, was methabenzthiazuron (Table 7). The pond at PO4 is connected to the drainage system but have no flow trough and should therefore only be affected by pesticide applications on the surrounding fields. No such use of methabenzthiazuron has been reported (J. Kreuger, personal communication). However there is always the possibility of accidental spills in the vicinity.

The pesticide found at the highest concentrations in the pond at PO4 in 1991 was DDT (Kreuger et. al 1999). DDT was withdrawn from the Swedish market in 1970 and totally banned in 1975. Still, 25 years later considerable amounts of DDT are found in the pond at PO4. The concentration was highest in the 0-2.5 cm and 2.5-10 cm sections, concentrations being 47 and 40 µg/kg dw respectively which is about half the amount found in bed sediment cores in 1991. The DDT concentration had not only decreased since 1991 but the DDT residues had also changed composition. Technical DDT is composed of on an average 80% p,p -DDT and 20% o,p –DDT, but after introduction to the environment it is degraded to its main metabolites p,p-DDE and p,p-DDD (Buffin 1998). Under anoxic conditions mainly p,p-DDD is formed while in the presence of oxygen mainly p,p-DDE is formed. In 1991 DDT residues found in the pond at PO4 were composed of 50% p,p-DDT, 40% p,p-DDD and 10% p,p-DDE. In April 2000 the DDT residues were composed of approximately 80% p,p-DDD and 20% p,p-DDE.

Table 7. Concentrations (µg/kg dw) of pesticides detected in bed sediment samples collected in the pond at PO4 in the central part of the catchment, together with concentrations of pesticides detected in bed sediment at PO4 in 1991 (Kreuger et. al 1999)

PO4	Year of collection and depth (cm)				
	2000				**1991**
Pesticide	Surface	0-2.5	2.5-10	10-12.5	0-10
DDT-p,p	<4^a	<3	<3	<3	**50**^{a}
DDT-o,p	<2	<2	<2	<2	n.d.^{b}
DDE-p,p	<4	**10**	**8**	**3**	**8**
DDD-p,p	**7**	**37**	**32**	**10**	**40**
diflufenican	*6*^{a}	<5	<5	<5	n.a
diuron	<20	<15	<1	**3**	n.d.
fenpropimorph	<90	<70	<1	<2	**40**
isoproturon	**13**	<25	<5	<7	n.d.
methabenzthiazuron	**181**	**274**	<15	<25	n.d.
permethrin	<9	<8	<9	<11	n.d.
pirimicarb	*18*	*14*	<3	<15	n.d.

^{a}Figures in bold are above the limit of determination (6 times the background noise), figures preceded by < are method detection limits (corresponding to 3 times the background noise), figures in italic are above the method detection limit but below the limit of determination and therefore only indicative
^{b} n.a.= not analyzed; n.d.= not detected

5.4.4 Surface and mobile sediments at LU12

The surface and mobile sediments at LU12 were comprised of silty clays and showed little textural variance during the collection period although waterflow in the stream decreased considerably. The glass jars used as sediment traps attracted benthic fauna, which were grossly removed before analysis. TOC in surface sediment at LU12 averaged 6.0%, ranging from 5.8 to 6.5% by dry weight with highest concentrations in June and August (Figure 6). TOC in mobile sediments at LU12 were somewhat higher but with considerably lower concentration (4.1%) in sediment collected during May-June (Figure 7).

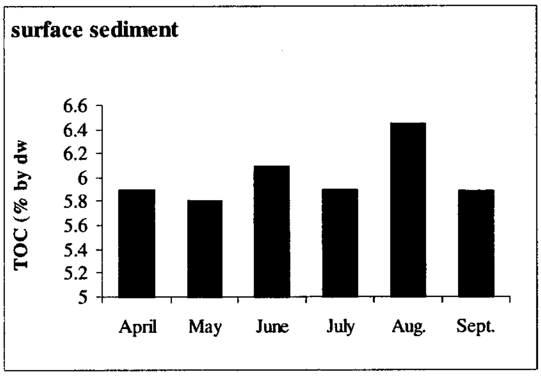

Figure 6. Total organic carbon content (TOC) in surface sediment collected once a month from April to September 2000 in the small pond at LU12 in the Vemmenhög catchment

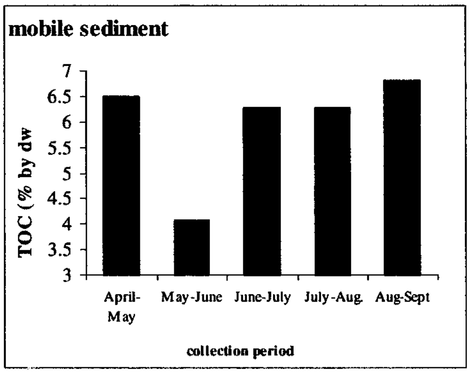

Figure 7. Total organic carbon content (TOC) in mobile sediment collected from April to September 2000 in the stream closely after the small pond at LU12 in the Vemmenhög catchment

Contrary to the results of e.g. Long et al. (1998) and Albanis et al. (1995) concentrations for most pesticides detected in surface and mobile sediments showed little temporal variation during the collection period (Tables 8 and 9). Neither were elevated amounts of pesticides found in periods following pesticide application and heavy rain, as is common for many pesticides detected in water in the area (Kreuger 1998, 2000, Kreuger & Hessel 1998*)*.

Table 8. Concentrations (µg/kg dw) of pesticides detected in surface sediment samples collected at LU12 from April to September 2000

surface sediment

Pesticide	April	May	June	July	Aug.	Sept.
DDT-p,p	**25**[a]	**5**	**28**	<2[a]	<3	<3
DDT-o,p	<2	<3	<3	<3	<1	<3
DDE-p,p	**7**	**5**	**5**	*4*[a]	**4**	**5**
DDD-p,p	<4	<3	<3	<3	<2	<3
diflufenican	**11**	**23**	**21**	**31**	**25**	**35**
diuron	**5**	**6**	**6**	**7**	**7**	**10**
esfenvalerate	**5**	**5**	**5**	**6**	**13**	**8**
fenpropimorph	**16**	<30	*16*	*9*	*11*	<30
isoproturon	**10**	**5**	**5**	**5**	**3**	**5**
methabenzthiazuron	**27**	<45	<45	<45	<5	<45
permethrin	*4*	<3	<2	<70	<5	<11
propiconazole 1[b]	*7*	**16**	**13**	**26**	**17**	<10
propiconazole 2[b]	<20	<45	<25	<60	<40	<10

[a] Figures in bold are above the limit of determination (6 times the background noise), figures preceded by < are method detection limits (corresponding to 3 times the background noise), figures in italic are above the method detection limit but below the limit of determination and therefore only indicative

[b] The pesticide consists of two different isomers in equal amounts but only one has been detected.

In many cases, the main source of pesticide contamination of sediments has been reported to be attributed to surface runoff following rain (e.g. Miles and Pfeuffer 1997, Knight and Cooper 1996). The lack of any trends over time for most of the detected pesticides is likely an effect of their strong sorption and slow movement in soil in addition with small contributions of pesticides from spills, spraydrift and surface runoff to the stream.during the season in 2000. There is also a possibility that the bulk of pesticides associated with particulate matter deposit somewhere before the stream reaches the pond at LU12. If this is the case the concentrations of most pesticides in surface and mobile sediment at LU12 is mainly a result of sedimentation and resuspension processes of sediments originating from the pond itself. In the investigation in 1990/91 (Kreuger et al. 1999) sediment samples were also collected in the Vemmenhög stream before it reaches the pond at LU12. The results implied that the bulk of the sedimentation occurred in the pond itself. Since then, however, the situation may have changed.

Table 9. Concentrations (µg/kg dw) of pesticides detected in mobile sediment samples collected at LU12 from April to September 2000, together with concentrations of pesticides detected in mobile sediment in 1990 (Kreuger et. al 1999)

mobile sediment	Collection period						
	2000					**1990**	**1990**
Pesticide	April-May	May-June	June-July	July-Aug.	Aug-Sept.	May-July	June-July
DDT-p,p	<3^{a}	<5	<7	<5	<6	n.d.^{b}	n.d.
DDT-o,p	<1	<1	<3	<1	<2	n.d.	n.d.
DDE-p,p	**4**^{a}	<3	<3	<3	<2	n.d.	n.d.
DDD-p,p	<3	<3	<3	<3	<4	n.d.	n.d.
diflufenican	**21**	**16**	**16**	**18**	**23**	n.a.^{b}	n.a.
diuron	**5**	**4**	**6**	**7**	<10	n.a.	n.a.
esfenvalerate^{c}	**3**	**2**	**3**	**3**	*5*^{a}	**70**	**60**
fenpropimorph	<25	*10*	<30	<30	<30	**200**	**200**
isoproturon	**19**	*4*	*3*	**5**	<3	n.d.	n.d.
propiconazole 1^{d}	*6*	*8*	*7*	<20	<20	**80**	**60**
propiconazole 2^{d}	<11	<10	<15	<20	<20		

[a] Figures in bold are above the limit of determination (6 times the background noise), figures preceded by < are method detection limits (corresponding to 3 times the background noise), figures in italic are above the method detection limit but below the limit of determination and therefore only indicative

[b] n.a.= not analyzed; n.d.= not detected

[c] The figure for 1990 refer to fenvalerate

[d] The pesticide consists of two different isomers in equal amounts but only one has been detected. Detection limits for the other isomer are shown in brackets

The only currently used pesticide showing any temporal variation during the sampling period was the herbicide isoproturon (Tables 8 and 9). Isoproturon is applied in the autumn together with diflufenican in a commercial product named Cougar. Interestingly, concentrations of diflufenican in mobile sediment at LU12 were quite stable during the sampling period while isoproturon concentrations decreased rapidly after initial high values in April, beginning of May. The differences potentially reflect the different intrinsic properties of these two pesticides. Isoproturon is the less hydrophobic of the two herbicides. Thus during high flow in April and May isoproturon should be more prone to leaching through the soil profiles to the drainage system, giving raise to high concentrations in the stream.

Surprisingly, p,p-DDT was detected in surface sediment at LU12 in April, May and June (Table 8). In July the p,p-DDT was no longer detected. The high p,p-DDT content as well as the fact that it is only found in the surface section of the bed sediment cores at LU12 (Table 5) indicated that the DDT had reached the environment quite recently and thus most probably by a single point source in direct or close contact with the pond. The sudden "disappearance" of DDT in July can not be explained easily but needs further investigation. The pesticide may either have travelled downstream with resuspended sediment as a result of heavy rains in the beginning of July, been buried by new settling sediment or are unevenly distributed in the pond at LU12 and therefore at times missed during sampling.

6. Conclusions

- The current investigation demonstrates the potential for stream and pond sediment to act as a sink for mainly hydrophobic pesticides. Although the findings of less hydrophobic pesticides in the sediments indicate that the hydrofobicity-related adsorption processes are not the only processes affecting sorption of pesticides to particulate material.

- The results from of pond sediment samples from sampling site PO4 and LU12 show the possibility of using bed sediments in the Vemmenhög area as historical 'fingerprints' of pesticide inputs to the freshwater ecosystem to reveal trends over time. To get a more accurate picture, however, there is a need of simple methods to determine the age of relatively young alluvial deposits.

- The input of single pesticides to the sediments in the pond in the Vemmenhög stream at LU12 as well as in the pond in the central parts of the catchment at PO4 seem to be declining, with a few exceptions.

- Contrary to pesticides detected in water from the Vemmenhög stream concentrations for most pesticides detected in surface and mobile sediments showed little temporal variation during the cropping season. This is likely an effect of their strong sorption and slow movement in soil in addition with small or insignificant contribution of pesticides from spills, spraydrift and surface runoff to the stream during the investigation period. It can, however, not be excluded that the bulk of pesticides associated with particulate matter deposit somewhere before the stream reaches the pond at LU12. There is, consequently, a need of further investigation of temporal and spatial sedimentation patterns and processes in the Vemmenhög stream.

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