



Determination of pesticides in ponds in an agricultural region in Sweden - sampling of water by solid-phase extraction

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by

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Abstract

Solid-phase extraction in the field is a beneficial and very convenient way of sampling water for pesticide analysis since it excludes voluminous and heavy water bottles and avoids adsorption of lipophilic pesticides on the sampling bottle. In this study atrazine, deltamethrin, diflufenican, esfenvalerate, ethofumesate, fenpropimorph, isoproturon, pirimicarb and terbutylazine were detected at low concentrations in ponds situated in Scania, south of Sweden. Sampling was conducted during May and June, 1999. Deltamethrin, esfenvalerate and lambda-cyhalothrin belong to the pyrethroids which are very lipophilic. These substances are therefore expected to adsorb on particles and other surfaces. No lambda-cyhalothrin was detected and very low concentrations of the other two pyrethroids. Sampling at the surface film of the water body as well as in the sediment might be necessary to detect higher concentrations of the pyrethroids. Nothing was detected on the particle fractions and in future studies it might be necessary to sample larger volumes of water in order to detect any particle bound pesticides. Isoproturon and ethofumesate were the most frequently detected pesticides, both are herbicides. Herbicides are the most regularly and heavily used pesticides. No absolute concentrations of pesticide detections can be reported from this study, since the method first needs more development and improvements. Primarily the performance of the internal standards needs to be improved.

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Determination of pesticides in ponds in an agricultural region in Sweden

- sampling of water by solid-phase extraction

1. Aim

The aim of this project was to use solid-phase extraction for the sampling of pesticides in water and to apply this method in the determination of pesticides in small ponds situated in agricultural fields in Scania, south of Sweden.

2. Introduction

An important field of study and research today is the fate and effect of pesticides in surface and groundwater. The concern in this subject has grown together with an increase in the use of pesticides during the second half of this century, even though the use in certain countries such as Sweden has decreased during the last few years. A particular reason for the current interest in this matter is that also modern pesticides find their way to surface and ground waters (Albanis *et al.*, 1994, Hessel *et al.* 1997, House *et al.*, 1997, Johansson, 1999, Kolpin *et al.*, 1998, Kreuger, 1998, Sundin, 1999; Vilsone, 1999). It is therefore necessary to regularly measure the environmental concentrations of pesticides to gain a better understanding of the fate of these chemicals as well as the potential exposure to non-target aquatic organisms. Pesticides are used primarily in agriculture, however they are also applied within industry, forestry, gardens and households. Other contributions of pesticides to the environment are accidental spills and dump sites. The total agricultural use of pesticides in Europe today is estimated to be about 350 000 tons of active ingredients (AI) per year, which is about 28% of the total use throughout the world (Kreuger, 1999). About 90 different active ingredients are registered for use within agriculture in Sweden, with a total of about 1600 tons (1998) of AIs applied each year (KemI, 1999). Pesticides make up a very diverse group of chemical compounds which contains great variation in structure, function, fate and toxicity.

There are many ways through which contamination and distribution of pesticides might occur, such as through atmospheric deposition, spray drift, runoff, leaching or direct overspray (Brown *et al.*, 1995, Torstensson, 1990; Wauchope & Leonard, 1980). Atmospheric transport followed by deposition is an important transport route for pesticides, which includes both limited transport and transport to areas far from the source (Kreuger, 1999). Wind drift of pesticides is a well-known problem. During the application of pesticides considerable amounts fail to reach the target but are instead distributed to the atmosphere as spray drift. It is possible to find pesticides 100 m from the spray site even when the wind speed is low (Arvidsson, 1987). The substance can in addition to wind drift move with water on the soil surface or within the ground both in the saturated as well as in the non-saturated zone (Torstensson, 1990). The presence and mobility of water is of major importance for the transport of pesticides and other substances. The amount of pesticides transported to surface water also depends on the chemical and physical properties of the compound. Important properties for mobility are water solubility, vapour pressure, dissociation constants and partition constants between soil-water (K_d , K_{oc}), water-air (K_w) and octanol-water (K_{ow}) (Kolpin *et al.*, 1998; Torstensson, 1990). The method and timing of application, including wind conditions and precipitation during and after application, is also of major importance for the detection of pesticides in surface waters.

The soil type affects the occurrence of pesticides in drainage water, e.g. losses from clay soils are small (<0.1%; Torstensson, 1988). However dry clay soils are often subjected to cracking leading to heavy bypass flow. Cracks are examples of macro-pore flow, which also includes pores such as worm holes and root channels. Bypass flow has been shown to be important in transporting chemicals to depths not possible if only matrix flow was in operation. The hydrology of the soil will determine rates and pathways of water flow and hence determine the transport of solutes such as pesticides (Brown *et al.*, 1995).

The degree of decomposition and adsorption of the pesticide to soil organic matter (Torstensson, 1990) as well as uptake of the substance into plants (Torstensson, 1988) are courses of events capable of affecting the degree of leakage of pesticides to surface water. The development of pesticides goes from less toxic but persistent substances towards more toxic but less persistent chemicals. Even though such modern synthetic substances disappear from the water body shortly after the distribution to the environment, peak concentrations of short duration might still have detrimental effects on the biota. One example is the synthetic pyrethroids, a group of insecticides, which biodegrade rather fast compared to many other pesticides (KemI, 1999). Pyrethroids are very lipophilic and adsorb easily to particles in the water (Sharon & Solomon, 1981; Andersson, 1999). Pyrethroid substances are in some cases therefore possible to detect in a water body only within hours after the application (Caquet *et al.*, 1992). In contrary, the herbicide atrazine which primarily was used to keep weeds off farmyards and surfaces in urban environments is banned in Sweden since 1989 (KemI, 1999) but it is still possible to detect residues in Swedish water environments (Kreuger, 1998, Sundin, 1999; Vilson, 1999).

Scania is situated in the very south of Sweden. It is rather densely populated and has intensive agriculture since the soils are very fertile and the climate is profitable. It constitutes about 2.5% of Sweden's area and has approximately 18% of the total agricultural area in Sweden (SCB, 1996). Half of the total load of AIs applied in Sweden are used in Scania (Kreuger, 1999). This results in a potential risk of pesticide contamination of aquatic environments in Skåne. Many agricultural areas in Scania have ponds situated in the fields. These ponds often have a diverse flora and fauna and are therefore important habitats for many organisms in the otherwise rather species poor agricultural environment. Due to the location of these ponds the risk of contamination is high and it is therefore important to document the presence of pesticides and other substances in this water environment.

In this study of pesticide occurrence in Scania the following species were chosen for detection: atrazine, deltamethrin, diflufenican, diuron, esfenvalerate, ethofumesate, fenpropimorph, hexazinon, isoproturon, lambda-cyhalothrin, metamitron, pirimicarb, propiconazole, simazine and terbutylazine. Lambda-cyhalothrin, pirimicarb, esfenvalerate and deltamethrin are insecticides, fenpropimorph and propiconazole are fungicides and the remaining substances are herbicides (Tomlin, 1997). These pesticides are widely used or still occurring in nature. Atrazine, diuron, hexazinon and simazine are examples of substances that are banned in Sweden (KemI, 1999). The chosen pesticides can be sampled and extracted together and they are relatively easy to analyse (P. Woin, personal communication). Sampling was conducted during May and June 1999.

Herbicides are among the most heavily and regularly used pesticides within agriculture (Kolpin *et al.*, 1998). Due to different and irregular weather conditions, the use of insecticides and fungicides vary within and between years and areas.

In addition to the aim of monitoring pesticides in ponds in Scania, an important part of this study considers a new kind of sampling device using direct solid-phase extraction of water in field. A vacuum was created in the field enabling water to be directly led over a solid-phase column. When water can be led through the solid-phase in field there is no need to first take the water sample in a glass or plastic bottle. This sampling device facilitates sampling as voluminous and heavy water bottles are excluded. Avoiding encapsuling of the water sample in a bottle is also important since it eliminates adsorption of lipophilic pesticides on the glass or plastic surface of the bottle. Rapid and strong adsorption to surfaces of the sampling device may result in decreased concentrations detected. Since this sampling method reduces losses of lipophilic pesticides, errors in the sampling method should be reduced.

In the analysis of pesticides and other chemical substances it is necessary to use standards for the quantification. Normally internal standards are added to the water after sampling. In this study where no water samples are collected in bottles but on solid-phase columns it complicates the addition of internal standard. Either the standard could be added to the column before sampling, or internal standards could be excluded and only external standards used in the calculations. Both methods are used in this study, since it is important to find a secure and reliable method for the quantification of pesticides in water using solid-phase extraction.

3. Material and methods

3.1 The ponds

Water samples were taken in 18 different ponds of which five ponds acted as controls, considered to be more or less unaffected by pesticide applications. All ponds are situated in an area in the south of Scania, in the very south of Sweden (Appendix 1). Many of the ponds are old marl-pits. The ponds differ a lot in appearance and the crops surrounding them vary (Table 1).

Table 1. Standing crops at time of sampling on the fields surrounding each pond where water samples were collected. The location of each pond is shown in Appendix 1.

Sample location (pond)	Standing crops at time of sampling
P1	Sugar beets 100%. Drains a neighbouring field with barley. Buffer zone.
P2	Barley 100%. Drains neighbouring field with beets. No buffer zone.
P3	Oilseed rape 60%. Buffer zone.
P4	Cereals, potatoes, vegetables.
P5	Oilseed rape 100%.
P6	Barley 100%.
P7	Wheat 100%. Buffer zone.
P8	Lies fallow.
P9	50% barley. 25% wheat. Buffer zone.
P10	Oilseed rape 100%.
P11	70% wheat. 30% Sugar beets.
P12	Peas 50%, 50% lies fallow. Buffer zone.
P13	Cereals, might also drain oilseed rape.
C1	Control, pasture.
C2	Control, pasture.
C3	Control, pasture.
C4	Control, pasture.
C5	Control, pasture.

3.2 Sampling

Sampling started on 5 May 1999, when the farmers had commenced their spring application of pesticides. Sampling was performed irregularly such as after rain or evident pesticide applications. The last sampling day was on 1 July 1999. All samplings are shown in table 2. One sample was taken in each pond at a time and samples were not taken in all ponds at each sampling occasion.

Table 2. Sampling locations and date of sampling in each pond.

Sampling location	5-6 May	12 May	17-19 May	31 May	2 June	4 June	7-8 June	15-16 June	27-28 June	30 June	1 July
P1	x	x	x		x		x	x		x	
P2	x		x		x		x	x		x	
P3	x	x	x		x						
P4									x		
P5	x		x								
P6	x	x	x	x			x	x		x	
P7	x	x	x	x			x	x		x	
P8	x		x								
P9	x		x			x		x			x
P10	x		x		x	x	x	x	x		
P11	x		x		x	x	x	x	x		
P12	x		x		x		x	x			
P13	x										
C1									x		
C2	x							x			
C3	x		x					x			
C4	x										
C5	x										

Sampling was conducted using solid-phase extraction in field (Figure 1). A solid-phase column was connected to a filter holder with a glass micro fibre filter. The water passed the filter and the filter holder before it was sucked through the column. A five metres long teflon tube connected the column with a vacuum flask and a pump. The pump, a rebuilt bicycle pump with reversed function, evacuated the system. The water was collected in the vacuum flask and the volume was measured using a graduated glass. A minimum of 500 ml was taken for each sample. The filter holder and the column were placed on a raft to keep it floating. Sampling was thereby conducted at a water depth of approximately 10 cm.

The filter holder and all connections were made of teflon to avoid adsorption of pesticides to these parts and to reduce the amount of disturbing substances from the material. Since there were some problems to make the system airtight a thin ring packing of a silica material was placed on top of the filter in the filter holder. How this packing affected the detection of the pesticides has not been further examined. The raft was made of foamed polystyrene.

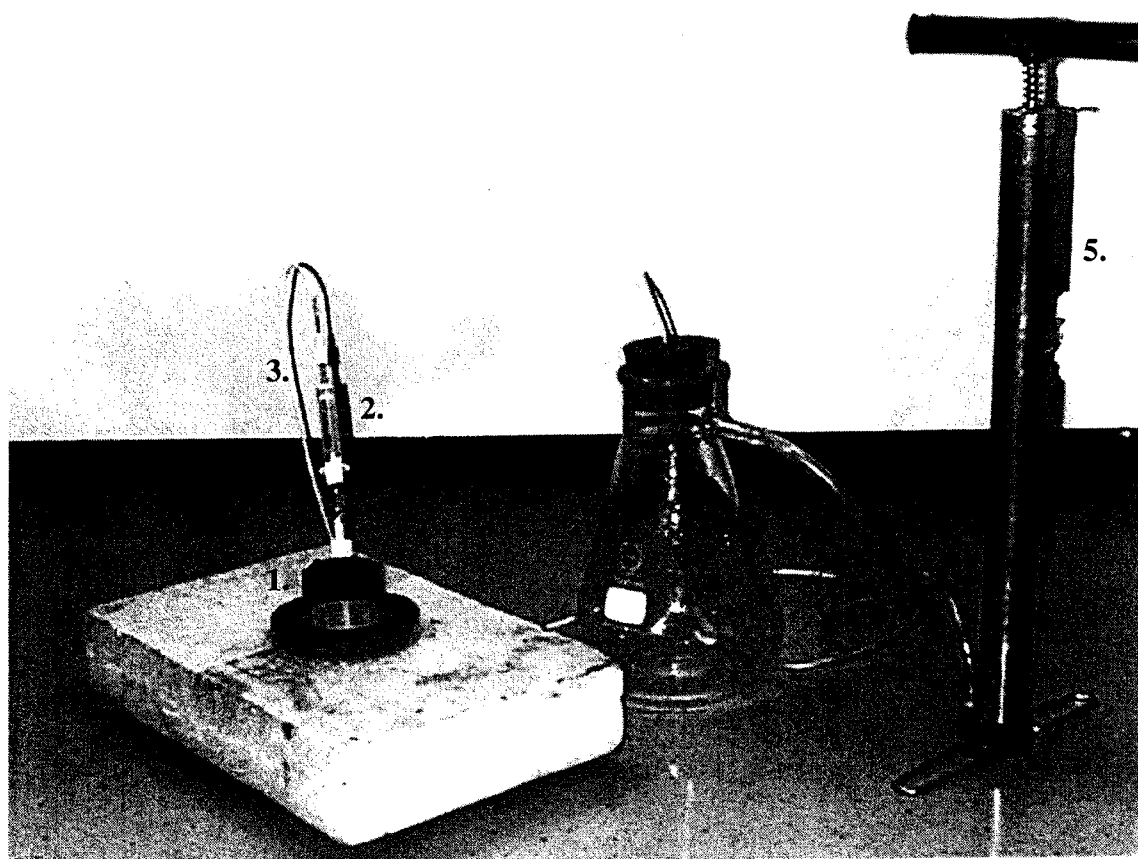


Figure 1. Sampling equipment. Water was drawn through the filter holder (1), the column (2), the tube (3) and was finally collected in the vacuum flask (4). A bicycle pump (5) with reversed function evacuated the system.

3.3 Standards and solvents

Internal standards were used to compensate for losses during sample handling, differences in recovery from different columns and filters as well as differences and losses in the final gas chromatographic (GC-) determination. Ethion and parathion were used as internal standards for the water samples, permethrin for the filter samples. Ethion was added to the columns before sampling by letting 50 ml of ultra pure water containing 0.166 μg of ethion to flow through the columns. Parathion (0.1 μg) was added to the eluate before evaporation. Both ethion and parathion were used as internal standards for the water fractions. Parathion was added in the case of an ethion failure. Permethrin (0.56 μg) was added as internal standard in the analytical step of extraction of the glass fibre filters.

External standards were also used for quantification. These had three different concentrations of the 14 pesticides that were part of the study. All pesticides were provided by Dr. Ehrenstorfer GmbH, Augsburg, Germany. For the extraction processes dichloromethane, cyclohexane and acetone were used. Solvents were provided by KEBO lab, Spånga, Sweden and were all of pesticide grade.

3.4 Preparations of columns

The columns were pre-washed with 2x5 ml of dichloromethane followed by 5 ml of acetone and 10 ml of ultra pure water. After addition of ethion the columns were finally dried and wrapped in aluminium foil. The prepared columns were stored in room temperature until sampling.

3.5 Extraction equipment

Isolute SPE columns with an internal volume of 6 ml and a content of 200 mg of ENV+ (from Sorbent AB, Västra Frölunda, Sweden) were used. The polymer (ENV+) is a highly crosslinked polystyrene divinylbenzene. A vacuum manifold (Vac Elute from Analytichem International, today Sorbent AB, Västra Frölunda, Sweden) was used for elution flow control when needed.

3.6 Solid-phase extraction

Analytes were eluted from the columns using 2x3 ml of dichloromethane. The extract was dried through a filter with sodium sulphate. Cyclohexane (5 ml) was added and the sample was concentrated using a rotary vacuum evaporator until less than 1 ml of the extract remained. The volume was adjusted to 1 ml with cyclohexane/acetone (9:1).

3.7 Extraction of filters

The glass fibre filters had a diameter of 47 mm, cut-off 0.7 μm (Whatman GF/F, Cat No 1825047, Whatman International Ltd, Maidstone, England). The filters were not pre-treated in any way before sampling. After sampling all filters were wrapped in aluminium foil and were stored in a freezer until extraction. A Soxtec Avanti 2050 was used for extraction of the filters. The filters were placed in pre-washed cellulose thimbles and permethrin was added as internal standard. The pre-washing was carried out by running empty thimbles in the same extraction program and with the same type of solvent as for the samples. Dichloromethane/acetone (1:1, v/v) was used as solvent. The extraction was carried out in a two step procedure using a Soxtec Avanti 2050 automatic extraction system (Foss Tecator AB, Höganäs, Sweden). The sample was first immersed in boiling solvent to dissolve most of the soluble material (2h, 170 °C). In the second step the sample was raised above the solvent surface to permit efficient washing with solvent from the condensers (1h, 170 °C). After the extraction, residues of solvent were collected from the condenser valves (2 min). The extract was finally concentrated by evaporation for 2 minutes. The remaining extract was dried through a filter with sodium sulphate. Cyclohexane (5 ml) was added and the extract was concentrated using a rotary vacuum evaporator. The volume was adjusted to 1 ml with cyclohexane/acetone (9:1).

3.8 Instrumental and chromatographic conditions

Deltamethrin, diflufenican, esfenvalerate, lambda-cyhalothrin, metamidron and propiconazol in both particle fractions and water fractions were analysed on a Hewlett Packard modell 5890 gas chromatograph equipped with two 63 Ni electron-capture detectors and two columns (CP-Sil 19 CB and CP-Sil 5 CB with dimensions of 20m x 0.32mm i.d. and 0.25 μm film thickness provided by Chrompack Sverige AB, Nacka, Sweden) attached to the same injector. Injection volume was 2 μl and the injection was splitless. Injector temperature was 250 °C and detector temperature was 300 °C. Oven temperature was set to 90 °C for 1 min, increasing 30 °C/min to 180 °C and then 4 °C/min to 260 °C, where it was held for 12 min.

Standards were injected in the start, in the middle and in the end of each run consisting of maximum 24 samples. Results were evaluated from calibration curves where analyte concentration was a function of response of standards divided by the response of the internal standard or from calibration curves where analyte concentration was a function of response of external standards only. The calculated concentrations were corrected for recoveries of each substance from fortified river water. The fortified water had been filtrated, extracted through ENV+ columns and treated in the same manner as the samples.

Atrazine, diuron, ethofumesate, hexazinon, fenpropimorph, isoproturon, pirimicarb, simazine and terbutylazine were analysed on a Hewlett Packard model 5890 gas chromatograph attached to a mass spectrometer (MS). The GC was equipped with a CP-Sil 5 CB column with dimensions of 60 m x 0.25 mm i.d. and 0.25 µm film thickness provided by Chrompack Sverige AB, Nacka, Sweden. Injector temperature was 250 °C, injection volume was 2 µl and the injection film splitless. Oven temperature was set to 90°C for 1 min, increasing 30 °C/min to 210 °C and then 4 °C/min to 300 °C, where it was held for 8 min. The MS was a Hewlett Packard model 5970 and it was operated in the electron impact (EI) ionisation mode at 70 eV. Data were collected in the selected ion monitoring (SIM) mode with two or three ions per compound.

In an earlier study using fortified river water samples it was shown that for the substances detected by GC/MS only a small portion of diuron, fenpropimorph and hexazinone were found on particles while the remaining portion of these pesticides were only recovered from the water phase (Andersson, 1999). The lipophilic insecticides deltamethrin, esfenvalerate and lambda-cyhalothrin are detected on GC/ECD, therefore both water and particle fractions were run on GC/ECD. Since the pesticides detected on GC/MS were not expected to adsorb on particles (Andersson, 1999) only water fractions were run on GC/MS.

3.9 Study of recoveries of ethion from ENV+ columns after storage.

Ethion (0.166 µg of ethion in 50 ml of ultra pure water) was added to nine pre-washed ENV+ columns. The columns were dried and wrapped in aluminium foil. Three columns were kept for 19 days, three columns for 8 days and three columns for 1 day in room temperature before they were eluted with 2x3 ml dichloromethane. The eluates were treated in the same manner as above. Detection was conducted on a HP GC/ECD as above.

4. Results and discussion, internal standards

4.1 The success of ethion and parathion as internal standards

The recoveries of ethion in the samples where analytes were detected were low (37%) and had a large standard deviation (25). Parathion had much too high recoveries in the same samples (177%), also with a large variation (111). The recoveries of ethion and parathion were low and high, respectively, both by EC and MS detection.

Differences in recovery of ethion and parathion are reflected in the large differences between results calculated either against ethion or parathion. Since the recovery for ethion was low, this might result in concentration values of the analytes that are too high. Ethion, though, should compensate for losses during sample handling, differences in recovery from different columns as well as differences in the final gas chromatographic (GC-) determination, which is the reason to use internal standards in the first place. Parathion was added to the samples after elution from the solid-phase columns and compensates therefore

only for losses in the final GC-determination. In the same manner as ethion might give too high concentrations, calculations against parathion will doubtless result in much too low concentrations.

Calculation against external standards only, does not compensate for any losses at all during the sample handling and determination steps. Since the concentrations calculated against external standards are corrected for recoveries from fortified water, the final concentrations depend very much on those recoveries and there is most certainly a variation in recoveries between different waters. The recoveries from fortified water are calculated using ethion as internal standard. According to the US Environmental Protection Agency the total recovery of a particular pesticide should be between 70 and 130% to be accepted as an adequate analysis method. However the recoveries for atrazine (137%), diuron (56%), ethofumesate (202%), fenpropimorph (29%), hexazinone (175%), metamitron (66%), pirimicarb (144%) and simazine (131%) lie outside these limits (Appendix 2). All concentrations of ethofumesate are zero due to a recovery of 202 % from the fortified water. A correction of the concentrations for this percentage would result in negative concentrations.

An alternative method to quantify analytes in water samples is to use standard additions. Known quantities of the analyte are added to the unknown and the increased signal exposes how much analyte was in the original sample. This a good method when there are few unknown analytes but in this case with many analytes it might be too complicated.

Ethion, despite its low recoveries, might be the most reliable method, since it compensates for losses during sample handling and determination. The low recoveries of ethion in the samples might have parallel losses of the analytes, how much is not known and varies most probably between the samples.

4.2 Recoveries of ethion from columns after storage

Ethion loaded on columns kept for 1, 8 and 19 days before elution did not show any tendency to get lower recoveries after a longer storage (Table 3).

Table 3. Recovery of ethion from columns loaded with 0.166 µg ethion. The bold numbers are mean values of recoveries from columns kept for 1, 8 and 19 days in room temperature.

Number of days	Recovery of ethion (%)
1	16
1	11
1	23
mean value	17
8	17
8	22
8	16
mean value	18
19	17
19	17
19	25
mean value	20

Ethion did not seem to bind more tightly to columns stored for a longer time period, neither did it seem to be degraded during storage. This is an important conclusion since the columns used in field were washed and prepared in lab and it could take up to 20 days before they were used. Degradation of ethion might though have occurred after the sampling in field but before the columns were put in a freezer, which could take up to 24 hours. Other reasons for the low recoveries of ethion from the solid-phase columns could possibly be that the ethion did not bind tight enough to the sorbent but was washed out with the water, or that it was too tightly bound and therefore not fully eluted. Since the recoveries from the samples had a large standard deviation (25) while the variation between recoveries from the stored columns was small (4) the problem might lie in the storing of the samples after eluting. Another possible explanation for the varying recoveries of ethion is that the batches of columns differ. All columns used in this experiment came from the same batch, while those used in the field study came from several different batches.

The results from this study show that it is necessary to further develop this method and to try new internal standards as well as a documented safe method to load the columns with internal standard.

5. Results and discussion, pesticide detections

Since there are some uncertainties about the method and the reliability in the results, all pesticide concentrations reported from this study are just indications of pesticides occurring in the ponds. Nothing was detected in the particle fractions; all detected concentrations are from water fractions. Atrazine, deltamethrin, diflufenican, esfenvalerate, ethofumesate, fenpropimorph, isoproturon, pirimicarb and terbutylazine were detected in the ponds (Appendix 2).

The most frequently detected pesticides were the phenylurea herbicide isoproturon and the herbicide ethofumesate. These herbicides were also frequently detected in streams in Scania 1998 (Sundin, 1999). The highest concentration of isoproturon, 0.5 µg/L (ethion) was found at P1 on 12 May. In the streams in Scania concentrations of isoproturon of up to 1 µg/L were detected (Sundin, 1999). The highest concentration of ethofumesate detected in this investigation was 0.3 µg/L at P10 on 19 May. The highest detected concentration of ethofumesate in streams (Sundin, 1999) in 1998 was 0.09 µg/L.

The triazine herbicide atrazine and the fungicide fenpropimorph were also detected at several occasions. The remaining pesticides detected were mainly found on single occasions. Ethofumesate, isoproturon and atrazine were the only substances detected at concentrations >0.1 µg/L. Concentrations calculated against external standards are about 2-4 times lower than the concentrations calculated against ethion.

Pesticides were detected in two control ponds; C1 and C5. Ethofumesate was detected in C1 on 28 June and isoproturon on 6 May in C5. These results show that even though these ponds were not surrounded by cultured fields, they still receive some input of pesticides.

The fact that nothing was detected on the particle fractions is interesting since it has been shown that in particular the pyrethroids distribute to particles (Andersson, 1999).

Either there were no pyrethroids in the ponds to be sampled, or the concentrations on the particles might have been too low to detect. Another possibility is that the water volumes sampled were too small to contain enough particles for detection of particle bound pesticides.

Very low concentrations of pesticides in the environment are difficult to detect and large volumes of water need to be extracted and concentrated. In this study the mean volume of all samples collected in the ponds was 804 ml and the mean volume of the samples in which pesticides were detected was 796 ml.

The triazine and phenyl urea herbicides are the pesticide residues most frequently detected in surface and ground waters in Europe (Garmouma *et al.*, 1998). They have high water solubility which results in high mobility and enhances the risk of aquatic environmental contamination (Pantone *et al.*, 1992). Herbicides are particularly toxic to photosynthetic organisms since they are specifically intended to kill plants. The phenyl urea herbicide isoproturon was one of the most detected pesticides in this investigation (Appendix 2). Isoproturon is used against weeds in crops and could therefore be expected to occur in all kinds of cereals (Table 4). Cultivations of sugar beets was surrounding P1, which had the highest concentration of isoproturon. The year before wheat was cultivated at those fields. Isoproturon was also commonly occurring in samples from P9, and was detected twice in P2. P9 is to 75% surrounded by barley and wheat and the pond is situated downhill the fields, which facilitates run-off from the fields to the pond. P2 has barley around the pond however the pond also drains a sugar beet field. The herbicide ethofumesate used against weeds on beets was detected in P2, but also in many other ponds and the detections of ethofumesate were more random than those for isoproturon. P1, P2 and P9 had the highest number of detected concentrations throughout the sampling period (Appendix 2). The herbicide terbutylazine was only detected once, in P2 on 15 June and the insecticide pirimicarb was only detected in P2, on 1 July. Both terbutylazine and pirimicarb were detected at low concentrations; 0.04 and 0.03 µg/L (ethion). The detected pesticides and their fields of application within agriculture in Sweden are reported in table 4.

Table 4. The detected pesticides and their fields of application within agriculture in Sweden and tonnes of each AI detected in this study sold in Sweden during 1997 and 1998 (KemI, 1998).

Pesticide	Field of application within agriculture	Tonnes of AI sold during 1997 in Sweden	Tonnes of AI sold during 1998 in Sweden
Herbicides			
Atrazine	Not admitted in Sweden since 1989	-	-
Diflufenican	Weeds in autumn crops	12.9	8.0
Ethofumesate	Weeds in cultivations of sugar beets	12.5	9.4
Isoproturon	Weeds in crops	127.2	92.7
Terbutylazine	Weeds in cultivations of peas	1.7	2.7
Fungicides			
Fenpropimorph	Fungi attack on cereals	48.0	57.9
Insecticides			
Deltamethrin	Insects and mites on pasture	0.8	0.9
Esfenvalerate	Insects	1.3	1.8
Pirimicarb	Aphids on crops	2.6	8.4

Several of the examined ponds (P1, P3, P7, P9, P12) were surrounded by buffer zones, strings of unsprayed vegetation between the crops and the pond. This diminishes the drift of pesticides from the field to the water. Creation of a 3 m buffer zone decreases drift deposition on the pond by a minimum of 95% (de Snoo & de Wit, 1998). This indicates that creating unsprayed crop edges offers good possibilities for the protection of aquatic ecosystems. P2 had no buffer zone, while P1 and P9 had one of approximately 6 m. These three ponds, though, had the highest number of detections throughout the sampling period, indicating that the pesticides have been distributed to the ponds by e.g. run-off events.

6. Environmental significance

In order to make a proper risk assessment it is important to know both the exposure and the toxicity of the compound to relevant organisms in the environment. Ecological effects of pesticides on organisms are dependent on both peak concentrations as well as the duration of the exposure and there are many factors that control the toxicity of a substance to organisms. The effects of pesticides in surface water can be both acute short term toxicological as well as long term ecological changes in ecosystems, which was shown in a study of direct and secondary effects of fenvalerate (a pyrethroid) on the structure of pond ecosystems (Woin, 1998). After exposure of fenvalerate there were both immediate lethal effects in the community as well as indirect community changes. According to these results even non persistent pesticides may produce detrimental effects resulting in long-term changes at the ecosystem level. It is, however, short pulses of high concentrations of pesticides that primarily might result in long-term irreversible effects on the ecosystem.

Naturally, the effects vary between pesticides and ecosystems and most probably additive and synergistic effects occur (Marinovich *et al.*, 1996). This makes research on ecological effects of antropogenic pollutants very complicated and the mere presence of a pesticide in an aquatic environment is not necessarily an immediate threat or risk to the organisms inhabiting the water environment.

Water quality guidelines for the protection of aquatic environments in the Netherlands have been suggested for 70 different pesticides (Crommentuijn *et al.*, 1997). Maximum Permissible Concentration (MPC) and Negligible Concentration (NC) were given for some of the pesticides detected in this investigation (Table 5). These pesticides are atrazine, deltamethrin, isoproturon and pirimicarb. The NC-value was obtained by dividing the MPC-value by a factor of 100 to account for combination toxicity. Isoproturon calculated against ethion exceeds the MPC in P1 on 12 May, however calculated against external standard the concentration lies below the MPC but above the NC. The detected concentration of deltamethrin in P3 on 12 May exceeds the MPC calculated against ethion and external standard. The concentrations though are very low and the absolute differences small. The MPC for deltamethrin lies below the detection limit (Appendix 2) meaning that it is not possible to tell when concentrations below the detection limit exceed the MPC. This is the case also for many other toxic substances; the limits for ecotoxicological effects lie below detection limits. Even though nothing is detected in the samples there might still be effects on the biological life.

One way of measuring the toxicity of a compound is to study the effect concentration on a particular organism. EC_{50} is the concentration that has a certain effect on 50% of the organisms included in the test. The toxicity of ethofumesate to green algae (*Scenedesmus subspicatus*) measured as inhibition of the growth is considered to be very high (KemI, 1999), EC_{50} (96h); 60 $\mu\text{g/L}$. The highest detected concentration of ethofumesate in this study was 0.3 $\mu\text{g/L}$, which in comparison with the EC_{50} seems to be very low. EC_{50} and LC_{50} values (lethal concentration) are often several magnitudes larger than guideline concentrations such as those from the Netherlands, since they only report about the acute toxicity of a certain substance on a certain organism and are not considering combined effects or effects during a longer time span. The LC_{50} for deltamethrin on *Daphnia magna*; 5 $\mu\text{g/L}$ is considered to be very low by the Swedish Chemical Inspectorate (KemI, 1999) but is several magnitudes higher than the MPC given by Crommentuijn *et al.* (1997). This quite clearly shows the complexity in this matter and the importance of a good knowledge about what these figures give information about. Since synergistic effects are possible (Marinovich *et al.*, 1996), one can also speculate that several pesticides at non-detectable or low concentrations might result in detrimental effects on the ecosystem.

Table 5. Maximum permissible concentration (MPC) and Negligible concentration (NC) (Crommentuijn *et al.*, 1997) for four of the pesticides detected in the Skåne ponds. The highest detected concentrations of these four substances in the Skåne ponds are also shown in the table.

	MPC ($\mu\text{g/L}$)	NC ($\mu\text{g/L}$)	Highest detected conc. in the Skåne ponds ($\mu\text{g/L}$)
Atrazine	2.9	0.03	0.1
Deltamethrin	0.0003	0.000003	0.03
Isoproturon	0.32	0.003	0.5
Pirimicarb	0.09	0.0009	0.04

The pyrethroids esfenvalerate and deltamethrin were only detected once, in P3 on 12 May 1999. The ponds P3 and P5 were added to the study only with the purpose to find pyrethroids, since both these ponds are surrounded by oilseed rape. Rape crops are often attacked by certain insects and are therefore regularly subjected to insecticide treatments. Since the pyrethroids are rather easily degraded and adsorb to sedimenting particles as well as macrophytes and other surfaces, they disappear quickly from the water body. The half-life for deltamethrin in an aerobic environment is 11-72 days, and 33-35 days for esfenvalerate which is more slowly decomposed (KemI, 1999). Esfenvalerate is faster degraded on the water surface with a half-life of 1.1 to 2.5 days (KemI, 1999). In natural water after application of deltamethrin (twice the recommended dose), more than 50% was eliminated from the water body within 24 hours, due to adsorption to particles in the water (KemI, 1999).

The effects of adsorption of pyrethroids on particles was also shown in a study of mesocosms sprayed with deltamethrin. The remaining concentration after four days was only 0.1% of the initial concentration (Caquet *et al.*, 1992). The average concentration of deltamethrin only five minutes after spraying was 25% of the initial concentration (2 µg/L). The same pattern of esfenvalerate has been studied. No measurable concentrations of esfenvalerate was found neither after 24 hours in enclosures with initial concentrations of 0.01 to 1.0 µg/L, nor in enclosures after 48 hours with an initial concentration of 5.0 µg/L (Lozano *et al.*, 1992). This pattern in the fate of pyrethroids was confirmed in a study on the pyrethroid fenvalerate (Woin, 1996).

Pyrethroids have been detected in natural waters. Concentrations of esfenvalerate of up to 0.2 µg/L was detected in water from the catchment area of the Vemmenhögsså in the south of Sweden in 1994 (Kreuger, 1998). Since the pyrethroids adsorb to particles that are deposited on the bottom these substances are concentrated in the sediments of the ponds, where they are degraded much more slowly than in the water. Deltamethrin has hardly been degraded at all after 30 days in sediment (KemI, 1999). Many sediment living organisms might therefore be affected. The sediment could also act as a reservoir by continuously adding the chemical into the water (Muir *et al.*, 1985) which could result in a long-term, low-level exposure to sediment living organisms and possibly also pose long-term effects on the ecosystem. The pyrethroids and other pesticides might therefore have effects on the ecosystem even though they are not detected or are detected at very low concentrations.

In addition to adsorption of pyrethroids to particles they might be distributed to the surface film of the pond (Crossland, 1982), and the sampling device used in this experiment would therefore have missed those substances. Perhaps might other lipophilic substances adsorb to the surface film and could therefore have possible negative effects on organisms but not be sampled and detected in studies such as this one. In future investigations, sampling of the surface film might therefore be useful in order to get a more informative picture of pyrethroid effects in the aquatic environment.

Since an ecosystem is very complex and there are many interactions that take place it is impossible to study the effects of pesticides on the whole ecosystem. Therefore indicator species are used, on which toxicity tests are conducted. Many tests are made on different species of algae as well as zooplankton such as Daphnids. Naturally there is also an extreme variability in sensitivity to pesticides among different species. In a study on 13 species of algae tested with 19 different chemical compounds the interspecific differences in

sensitivity were as great as three orders of magnitude (Peterson *et al.*, 1994). No one species consistently emerged as the most sensitive, which discredited the concept of a universal indicator species. A large degree of variation among species to the different pesticides tested was obvious in the study, with the growth of some species being completely unaffected by compounds that were highly phytotoxic to other species.

There are numerous ecological implications of the varying sensitivity of algae to different pesticides. In the freshwater ecosystem algae are important primary producers in the food web, with phytoplankton providing food for a diverse community of zooplankton and filter feeders. Epiphytic and periphytic algae are grazed upon by gastropods and other invertebrates. Depending on the herbicide, water contamination could result in a die-off of most algal species present, causing complete disappearance of this food source. Alternatively certain species or groups of algae could be selectively inhibited causing a completely different pattern in effects.

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I have very much enjoyed my stay at the Department of Environmental Assessment which has been very informative and instructive for me. I wish to thank my supervisors Peter Sundin and Per Woin (Lund University) for getting me started as well as for their help and instructions during sampling and with corrections of the report. However, I especially want to thank Gunborg Alex, Eva Lundgren, Märith Peterson and Åsa Ramberg for all their help and support in the lab. They always had time for my questions and are also very good friends. Helén Andersson, my former colleague also helped me a lot and I want to thank her for excellent company as well as informative instructions, explanations and discussions!

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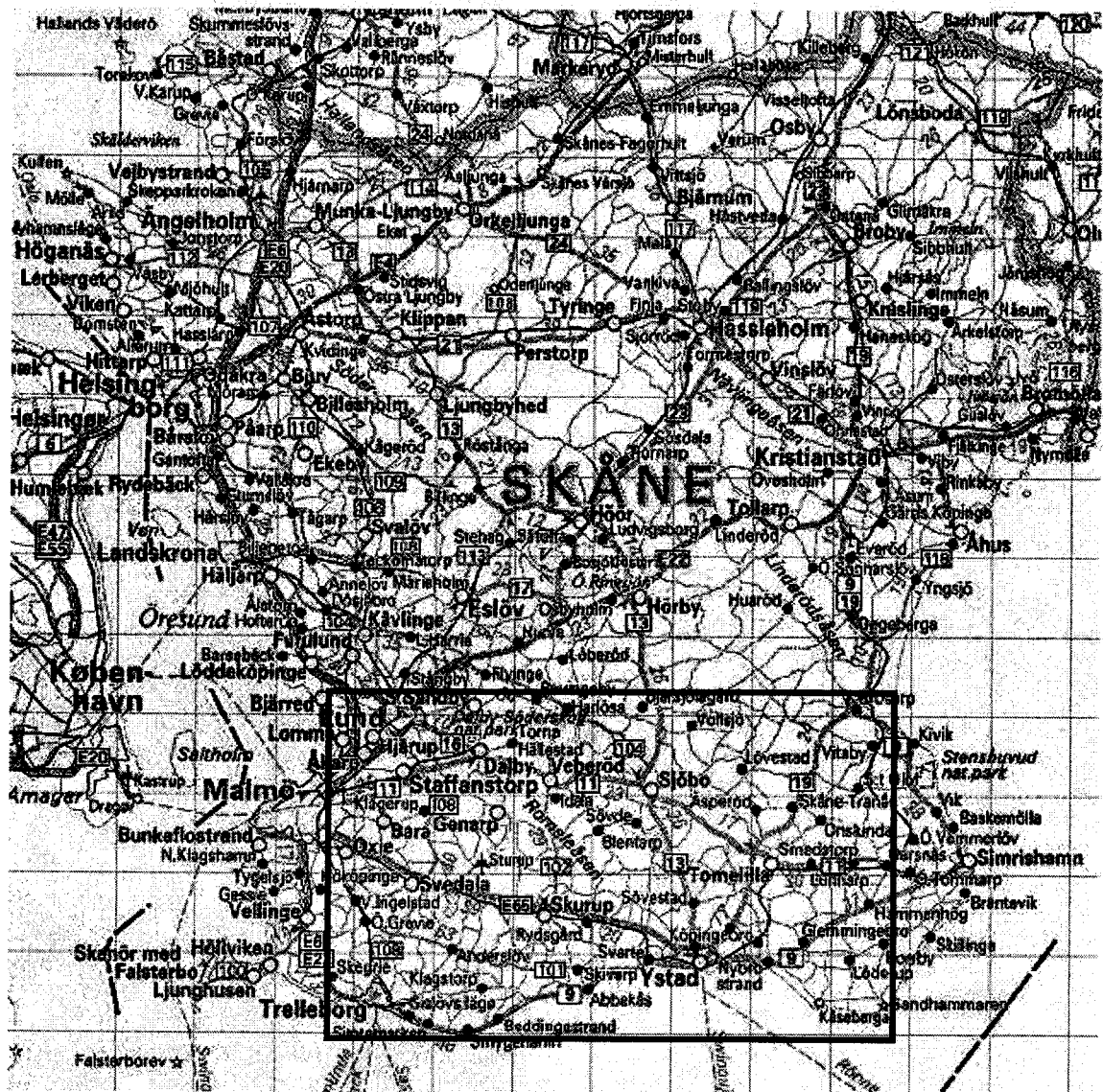
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Appendix 1

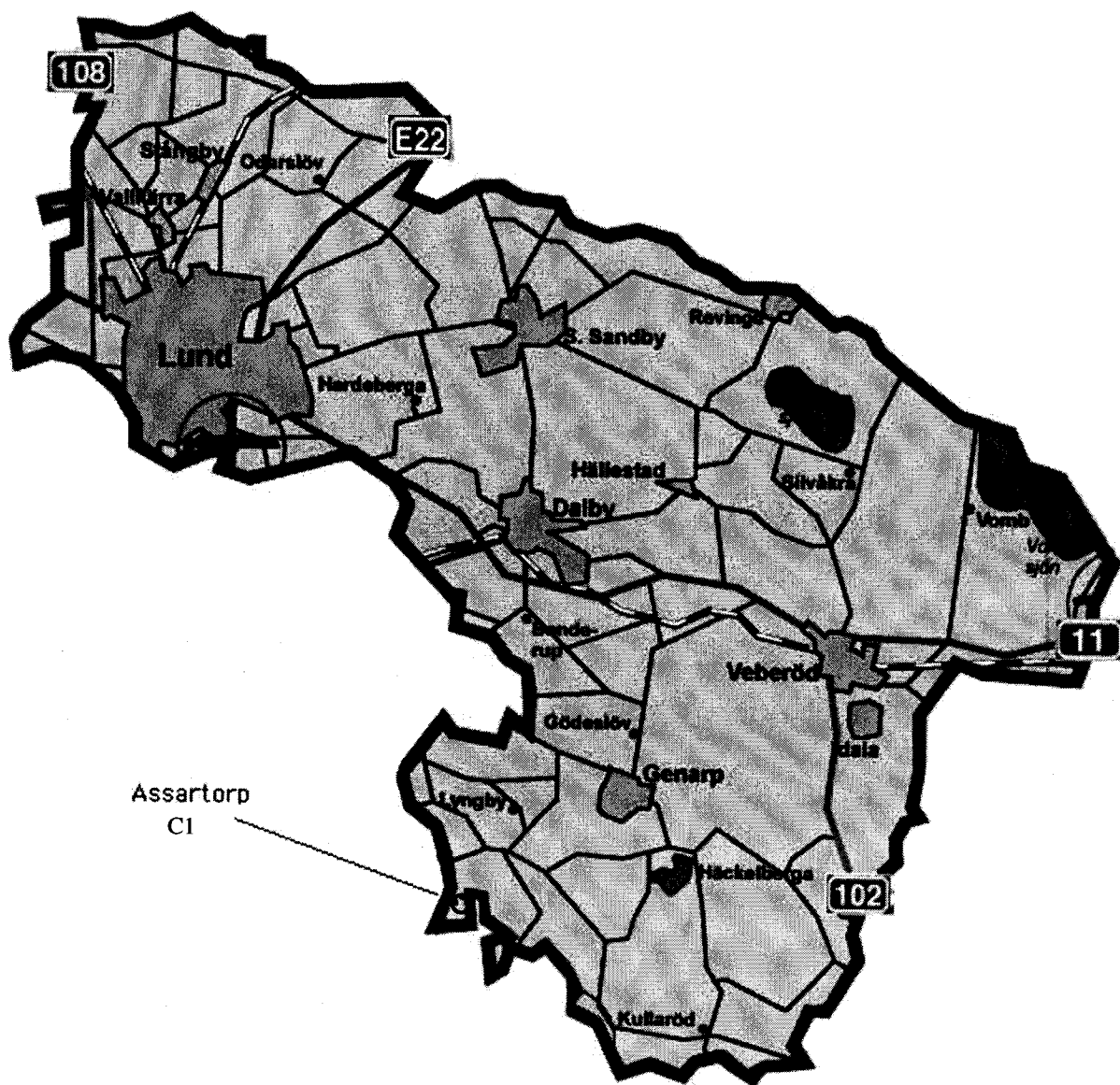
The names of the ponds in which sampling was conducted and their code notations used in the text.

Pond	Code notation
Alstad	P1
Apelhög	P2
Domme	P3
Hammars ränna	P4
Klörup	P5
Mölleberga 1	P6
Mölleberga 2	P7
Mölleberga 3	P8
Rövarbacken	P9
Önnarp 1	P10
Önnarp 2	P11
Önnarp 3	P12
Fjärshus	P13
Assartorp	C1
Borup	C2
Hyby	C3
Sövestad 1	C4
Sövestad 2	C5

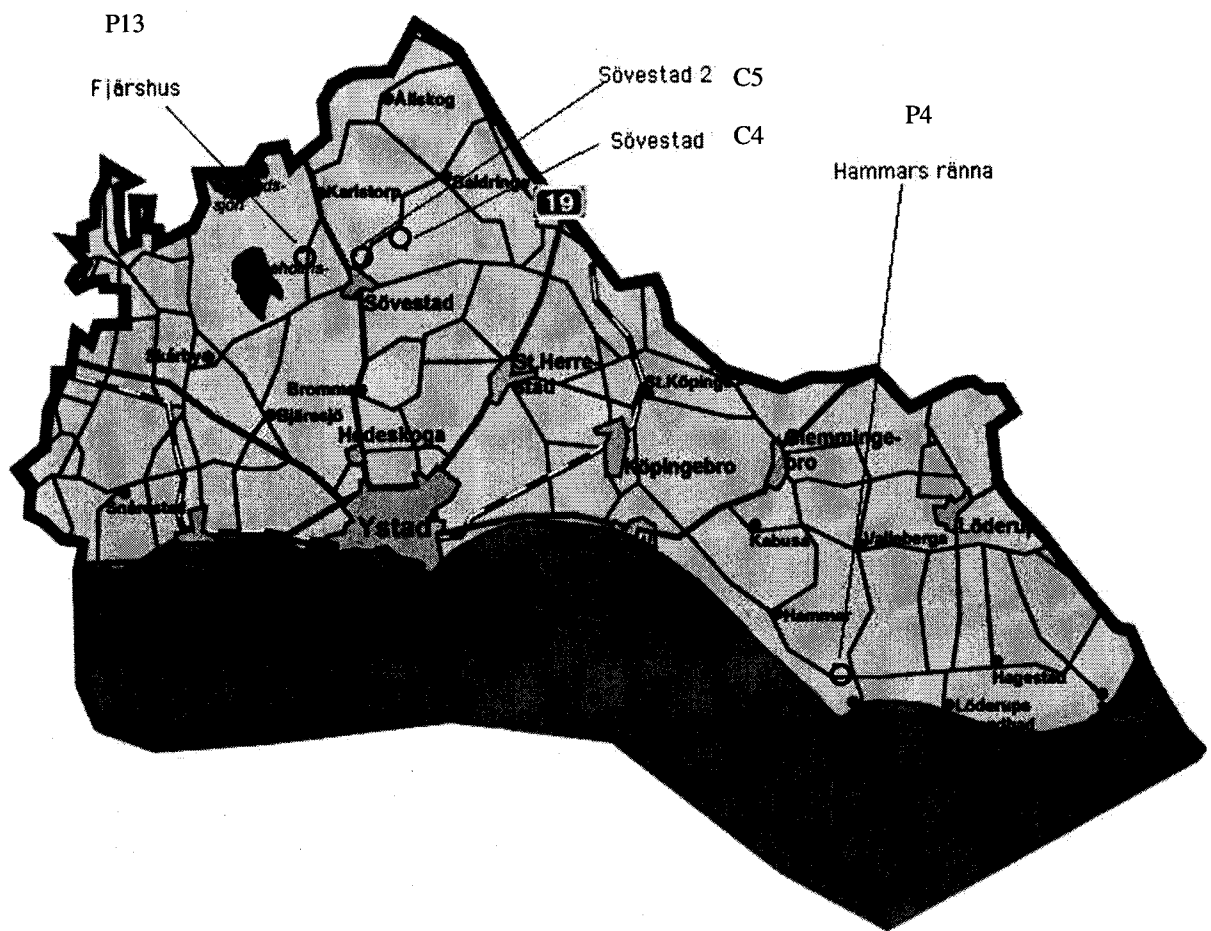
Map of Scania (Skåne), which is situated in the very south of Sweden. The square shows the area where sampling was conducted. The following maps show parts of this area more in detail.



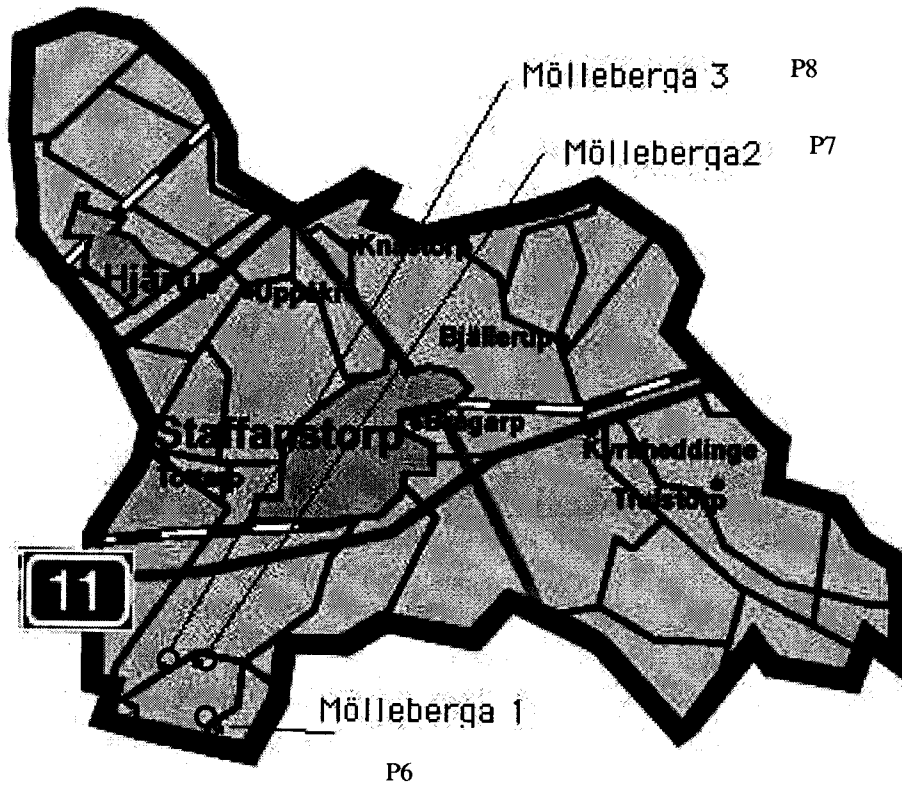
Map B, the Lund area



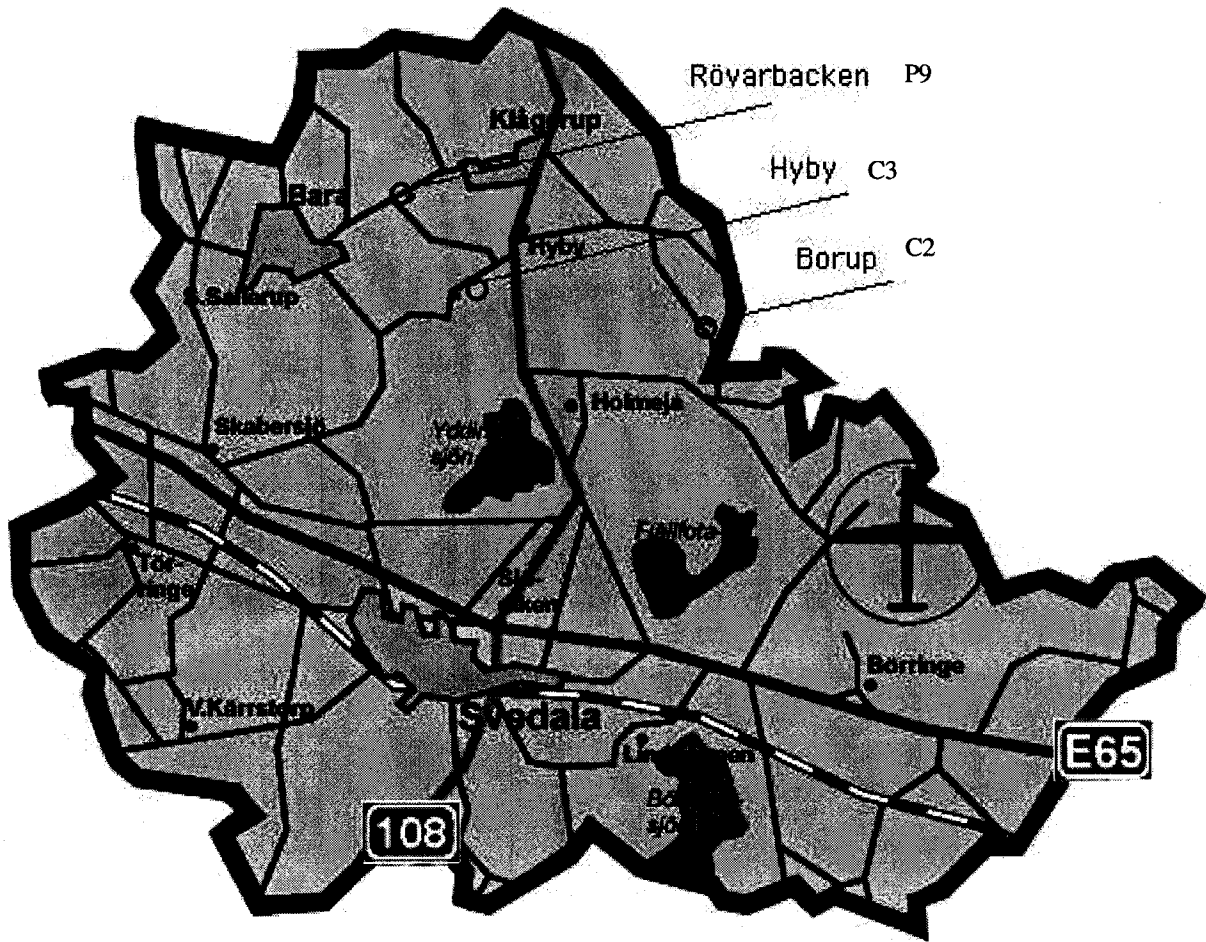
Map C, the Ystad area



Map D, the Staffanstorp area



Map E, the Svedala area



Appendix 2

Table over detected pesticides in the ponds included in the study.

	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	C1	C2	C3	C4	C5
atrazine	x	x					x					x						
deltamethrin			x															
diflufenican									x									
diuron																		
esfenvalerate			x															
ethofumesate		x		x		x		x	x	x	x			x				
hexazinone																		
isoproturon	x	x	x		x				x	x	x							x
lambda-cyhalothrin																		
metamitron																		
fenpropimorph	x					x	x											
pirimicarb		x																
propiconazole																		
simazine																		
terbutylazine		x																

Concentrations of detected pesticides in the ponds, 5 May to 1 July.
 The given concentrations are from calculation against ethion or parathion as internal standard,
 as well as against external standards only (corrected for recovery percentages from fortified water).

		ethion	parathion	external std	ethion	parathion	external std
		isoprot	isoprot	isoprot	ethofum.	ethofum.	ethofum.
Pond	Date	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)
P1	12-May	0.5	0.1	0.2	nd	nd	nd
P1	18-May	0.1	0.02	0.02	nd	nd	nd
P1	02-June	nd	nd	nd	nd	nd	nd
P1	07-June	nd	nd	nd	nd	nd	nd
P2	02-June	0.08	0.02	0.04	nd	nd	nd
P2	15-June	0.07	0.02	0.06	nd	nd	nd
P2	15-June	nd	nd	nd	nd	nd	nd
P2	01-July	nd	nd	nd	0.06	0.006	nd
P3	06-May	0.03	0.004	0.01	nd	nd	nd
P3	12-May	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	0.3	0.03	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P5	06-May	0.2	0.04	0.3	nd	nd	nd
P6	18-May	nd	nd	nd	0.1	0.03	nd
P6	16-June	nd	nd	nd	nd	nd	nd
P6	30-June	nd	nd	nd	0.06	0.01	nd
P7	16-June	nd	nd	nd	nd	nd	nd
P7	08-June	nd	nd	nd	nd	nd	nd
P8	05-May	nd	nd	nd	0.04	0.01	nd
P8	17-May	nd	nd	nd	nd	nd	nd
P9	05-May	0.06	0.01	0.03	nd	nd	nd
P9	17-May	nd	nd	nd	0.3	0.04	nd
P9	04-June	0.07	0.02	0.05	nd	nd	nd
P9	15-June	0.04	0.02	0.05	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	01-July	0.06	0.01	0.04	0.08	0.02	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P10	05-May	0.03	0.006	0.02	0.2	0.04	nd
P10	19-May	nd	nd	nd	0.3	0.06	nd
P11	05-May	0.1	0.01	0.02	nd	nd	nd
P11	19-May	nd	nd	nd	nd	nd	nd
P11	28-June	nd	nd	nd	0.1	0.01	nd
P12	07-June	nd	nd	nd	nd	nd	nd
C1	28-June	nd	nd	nd	0.07	0.02	nd
C5	06-May	0.02	0.005	0.01	nd	nd	nd

		ethion atrazine	parathion atrazine	external std atrazine	ethion terbutylazine	parathion terbutylazine	external std terbutylazine
Pond	Date	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)
P1	12-May	0.04	0.01	0.008	nd	nd	nd
P1	18-May	nd	nd	nd	nd	nd	nd
P1	02-June	nd	nd	nd	nd	nd	nd
P1	07-June	nd	nd	nd	nd	nd	nd
P2	02-June	0.04	0.008	0.01	nd	nd	nd
P2	15-June	0.1	0.04	0.05	0.03	0.01	0.01
P2	15-June	nd	nd	nd	nd	nd	nd
P2	01-July	nd	nd	nd	nd	nd	nd
P3	06-May	nd	nd	nd	nd	nd	nd
P3	12-May	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P5	06-May	nd	nd	nd	nd	nd	nd
P6	18-May	nd	nd	nd	nd	nd	nd
P6	16-June	nd	nd	nd	nd	nd	nd
P6	30-June	nd	nd	nd	nd	nd	nd
P7	16-June	nd	nd	nd	nd	nd	nd
P7	08-June	nd	nd	nd	nd	nd	nd
P8	05-May	nd	nd	nd	nd	nd	nd
P8	17-May	nd	nd	nd	nd	nd	nd
P9	05-May	nd	nd	nd	nd	nd	nd
P9	17-May	nd	nd	nd	nd	nd	nd
P9	04-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P10	05-May	nd	nd	nd	nd	nd	nd
P10	19-May	nd	nd	nd	nd	nd	nd
P11	05-May	nd	nd	nd	nd	nd	nd
P11	19-May	nd	nd	nd	nd	nd	nd
P11	28-June	nd	nd	nd	nd	nd	nd
P12	07-June	0.05	0.01	0.01	nd	nd	nd
C1	28-June	nd	nd	nd	nd	nd	nd
C5	06-May	nd	nd	nd	nd	nd	nd

		ethion fenprop.	parathion fenprop.	external std fenprop.	ethion pirimicarb	parathion pirimicarb	external std pirimicarb
Pond	Date	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)
P1	12-May	nd	nd	nd	nd	nd	nd
P1	18-May	nd	nd	nd	nd	nd	nd
P1	02-June	0.02	0.01	0.02	nd	nd	nd
P1	07-June	0.02	0.01	nd	nd	nd	nd
P2	02-June	nd	nd	nd	nd	nd	nd
P2	15-June	nd	nd	nd	nd	nd	nd
P2	15-June	nd	nd	nd	nd	nd	nd
P2	01-July	nd	nd	nd	0.04	0.006	0.002
P3	06-May	nd	nd	nd	nd	nd	nd
P3	12-May	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P5	06-May	nd	nd	nd	nd	nd	nd
P6	18-May	nd	nd	nd	nd	nd	nd
P6	16-June	0.02	0.02	0.04	nd	nd	nd
P6	30-June	nd	nd	nd	nd	nd	nd
P7	16-June	0.02	0.02	0.03	nd	nd	nd
P7	08-June	nd	nd	nd	nd	nd	nd
P8	05-May	nd	nd	nd	nd	nd	nd
P8	17-May	nd	nd	nd	nd	nd	nd
P9	05-May	nd	nd	nd	nd	nd	nd
P9	17-May	nd	nd	nd	nd	nd	nd
P9	04-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P10	05-May	nd	nd	nd	nd	nd	nd
P10	19-May	nd	nd	nd	nd	nd	nd
P11	05-May	nd	nd	nd	nd	nd	nd
P11	19-May	nd	nd	nd	nd	nd	nd
P11	28-June	nd	nd	nd	nd	nd	nd
P12	07-June	nd	nd	nd	nd	nd	nd
C1	28-June	nd	nd	nd	nd	nd	nd
C5	06-May	nd	nd	nd	nd	nd	nd

		ethion esfenval.	parathion esfenval.	external std esfenval.	ethion deltam.	parathion deltam.	external std deltam.
Pond	Date	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)
P1	12-May	nd	nd	nd	nd	nd	nd
P1	18-May	nd	nd	nd	nd	nd	nd
P1	02-June	nd	nd	nd	nd	nd	nd
P1	07-June	nd	nd	nd	nd	nd	nd
P2	02-June	nd	nd	nd	nd	nd	nd
P2	15-June	nd	nd	nd	nd	nd	nd
P2	15-June	nd	nd	nd	nd	nd	nd
P2	01-July	nd	nd	nd	nd	nd	nd
P3	06-May	nd	nd	nd	nd	nd	nd
P3	12-May	0.04	0.01	0.009	0.03	0.007	0.008
P4	27-June	nd	nd	nd	nd	nd	nd
P4	27-June	nd	nd	nd	nd	nd	nd
P5	06-May	nd	nd	nd	nd	nd	nd
P6	18-May	nd	nd	nd	nd	nd	nd
P6	16-June	nd	nd	nd	nd	nd	nd
P6	30-June	nd	nd	nd	nd	nd	nd
P7	16-June	nd	nd	nd	nd	nd	nd
P7	08-June	nd	nd	nd	nd	nd	nd
P8	05-May	nd	nd	nd	nd	nd	nd
P8	17-May	nd	nd	nd	nd	nd	nd
P9	05-May	nd	nd	nd	nd	nd	nd
P9	17-May	nd	nd	nd	nd	nd	nd
P9	04-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	15-June	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P9	01-July	nd	nd	nd	nd	nd	nd
P10	05-May	nd	nd	nd	nd	nd	nd
P10	19-May	nd	nd	nd	nd	nd	nd
P11	05-May	nd	nd	nd	nd	nd	nd
P11	19-May	nd	nd	nd	nd	nd	nd
P11	28-June	nd	nd	nd	nd	nd	nd
P12	07-June	nd	nd	nd	nd	nd	nd
C1	28-June	nd	nd	nd	nd	nd	nd
C5	06-May	nd	nd	nd	nd	nd	nd

		ethion	parathion	external std
		diflufenican	diflufenican	diflufenican
Pond	Date	Conc (ug/L)	Conc (ug/L)	Conc (ug/L)
P1	12-May	nd	nd	nd
P1	18-May	nd	nd	nd
P1	02-June	nd	nd	nd
P1	07-June	nd	nd	nd
P2	02-June	nd	nd	nd
P2	15-June	nd	nd	nd
P2	15-June	nd	nd	nd
P2	01-July	nd	nd	nd
P3	06-May	nd	nd	nd
P3	12-May	nd	nd	nd
P4	27-June	nd	nd	nd
P4	27-June	nd	nd	nd
P5	06-May	nd	nd	nd
P6	18-May	nd	nd	nd
P6	16-June	nd	nd	nd
P6	30-June	nd	nd	nd
P7	16-June	nd	nd	nd
P7	08-June	nd	nd	nd
P8	05-May	nd	nd	nd
P8	17-May	nd	nd	nd
P9	05-May	nd	nd	nd
P9	17-May	nd	nd	nd
P9	04-June	nd	nd	nd
P9	15-June	nd	nd	nd
P9	15-June	0.03	0.01	0.01
P9	01-July	nd	nd	nd
P9	01-July	0.05	0.01	0.009
P10	05-May	nd	nd	nd
P10	19-May	nd	nd	nd
P11	05-May	nd	nd	nd
P11	19-May	nd	nd	nd
P11	28-June	nd	nd	nd
P12	07-June	nd	nd	nd
C1	28-June	nd	nd	nd
C5	06-May	nd	nd	nd

Recovery of ethion and parathion from samples with detected analytes.

		ethion	parathion
Pond	Date	recovery (%)	recovery (%)
P1	12-May	29	135
P1	18-May	16	101
P1	02-June	28	74
P1	07-June	32	143
P2	02-June	51	231
P2	15-June	77	233
P2	15-June	40	102
P2	01-July	12	133
P3	06-May	25	323
P3	12-May	25	84
P4	27-June	15	124
P4	27-June	18	109
P5	06-May	139	682
P6	18-May	49	170
P6	16-June	63	162
P6	30-June	22	130
P7	16-June	47	135
P7	08-June	45	167
P8	05-May	33	178
P8	17-May	19	90
P9	05-May	42	223
P9	17-May	22	187
P9	04-June	78	241
P9	15-June	18	246
P9	15-June	42	86
P9	01-July	64	237
P9	01-July	29	96
P10	05-May	61	311
P10	19-May	16	81
P11	05-May	18	178
P11	19-May	19	93
P11	28-June	18	222
P12	07-June	24	123
C1	28-June	36	161
C5	06-May	32	149

Recoveries of the analysed pesticides corrected for the recovery of ethion from analysis of fortified water.

Pesticide	Recovery (%)
atrazine	137
deltamethrin	70
diflufenican	84
diuron	56
esfenvalerate	72
ethofumesate	202
hexazinone	175
isoproturon	88
lambda-cyhalothrin	78
metamitron	66
fenpropimorph	29
pirimicarb	144
propiconazole	99
simazine	131
terbutylazine	160

Approximate detection limits for the pesticides analysed.

Pesticide	Detection limit (ug/L)
atrazine	0.01
deltamethrin	0.04
diflufenican	0.04
diuron*	0.01
esfenvalerate	0.04
ethofumesate	0.02
fenpropimorph	0.02
hexazinon*	0.03
isoproturon	0.01
lambda-cyhalothrin*	0.04
pirimicarb	0.01
propiconazole*	0.03
simazin*	0.02
terbutylazine	0.02

* Pesticides not detected in the investigation