



Jenny Kreuger, Stina Adielsson & Henrik Kylin

Monitoring of pesticides in atmospheric deposition in Sweden 2002-2005

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Short summary

- Currently used pesticides were regularly detected at ng/l-levels in rainwater in Sweden, with maximum concentrations up to 0.8 µg/l for single compounds.
- A total of 47 substances were detected, 26 of these being herbicides, 8 fungicides, 8 insecticides and 5 metabolites.
- A significant contribution to atmospheric deposition in southern Sweden from pesticides that are no longer registered for use within Sweden. Up to 18 different compounds originating from outside of Sweden were detected, with eight of these occurring during all four years.
- Total seasonal deposition from currently used pesticides in southern Sweden ranged between 300-1 000 mg/ha. Deposited amounts correspond to ca 0.01-0.0004% of applied dose on Swedish fields.
- Concentrations in rainfall exceeded occasionally the preliminary Swedish target values to protect surface water quality for five of the pesticides.
- There is a correlation between origin of air-masses and composition of detected pesticides.
- The concentrations of lindane, now banned within the EU, are decreasing as compared to the beginning of the 1990s.

Recommendations for future work:

* Additional monitoring sites

A single monitoring site presents uncertainties in the actual deposition loads and of how representative they are for larger regions, including a south-north gradient.

* A longer sampling season

The current monitoring program is limited to a four-month period. However, the application season starts earlier and ends later in Continental Europe than in Sweden, including many volatile fungicides and insecticides being applied during the summer months, e.g. in fruit orchards and wines, when no collection of deposition is done in the current programme. It would also be beneficial for the interpretations if more samples could be taken and with a higher frequency.

* Inclusion of additional pesticides

To select additional pesticides based on their intrinsic properties (mainly vapour pressure, half-life in air and persistence) and used amounts in Europe (the review also suggesting pesticides that could be excluded from the analytical list). There are some 400 different pesticides applied throughout Europe. The least investigated environmental fate processes today is atmospheric transport. Little is known of atmospheric half-lives and degradation processes in the air.

* Air sampling

A programme that also included air (gas and particle phase) sampling and dry deposition would give information on transport mechanisms.

Introduction

Large amounts of pesticides are used each year within agricultural production all over the globe. In Europe alone pesticides are sold to an annual value of US \$7.5 billions, which is a quarter of the global market. Pesticides play a crucial role in ensuring good harvest and a safe food supply, but during recent decades a growing concern about the environmental fate and impact of pesticides residues has emerged. Pesticides might be transported away from treated areas and monitoring studies have demonstrated the widespread occurrence of modern, agricultural pesticides in surface water, ground water, sediments and biota. They can also enter into the atmosphere, via spray drift, volatilisation or wind erosion. In the atmosphere the substance will either be in the gas phase, particle bound, or dissolved in the water phase (rain and water droplets). The surface film of the droplets may also play a role in the partitioning process between the gas phase and the water phase. The tendency of a substance to enter the atmosphere, and how it is partitioned between gas, particle, and dissolved phase, depends on its physical and chemical properties as well as on the method of application and formulation.

In the atmosphere pesticides can be transported over long distances, leading to deposition in remote areas (e.g. Chernyak et al., 1996; van Dijk & Guicherit, 1999; Dubus et al., 2000; Hermanson et al., 2005; Kreuger & Staffas, 1999; Majewski et al., 2000; Rice & Chernyak 1997). Pesticide concentrations in precipitation can show large seasonal variations such that concentrations are higher during the spraying season, indicating short-range transport (Dubus et al., 2000). Pesticides occurring in precipitation all over the year and with a more even distribution are expected to be subject to long-range transport. In a European review study Dubus et al. (2000) states that concentrations are normally higher, ranging up to a few micrograms per litre for substances subject to short-range transport (also supported by van Dijk & Guicherit, 1999).

Lindane (including alpha- and beta-HCH) and atrazine are substances frequently detected in remote areas and are evidently transported over long distances (Blanchoud et al., 2002; Duyzer, 2003; Ellerman et al., 2005; Eppel et al., 2002; Lode et al., 1995; Siebers et al., 1994; Wania & Haugen, 1999). These two substances and their metabolites are also the most commonly analysed (Dubus et al., 2000). Other substances that are commonly found in precipitation in Europe are alachlor, dichlorprop, isoproturon, MCPA and terbuthylazine (Bossi et al., 2002; Bucheli et al., 1998; Charizopoulos & Papadopoulou-Mourkidou, 1999; Ellerman et al., 2005; Lode et al., 1995; Siebers et al., 1994).

Sampling of both dry and wet deposition on the west coast of Sweden have been reported (Brorström-Lundén et al., 1994; Brorström-Lundén, 1996). However, in these studies the focus was on PCB, HCH, HCB and PAH only, and they did not include any currently-used pesticides. During three years in the beginning of the 90's Kreuger & Staffas (1999) sampled precipitation at three sites, one in the very south, one not far from Stockholm and one in the very north of the country. At the two southern sites HCHs, phenoxy acids and triazines were the substances most commonly found. Of the substances banned in Sweden, 2,4-D and atrazine were found in 50% of the samples. In the northern site HCHs were commonly detected but at lower concentrations, phenoxy acids and atrazine were found occasionally, all at lower concentrations than in the southern sites. The result indicates long-range transport of some pesticides to Sweden.

There have been measurements of wet deposition at two locations included in the Danish programme for environmental monitoring (Ellerman, 2005). Twenty substances were analysed and 19 of them were found. The total annual deposition at the two sites were 31.1 and 65.5 $\mu\text{g}/\text{m}^2$, respectively, with the largest contribution at both locations from pendimethalin (12-28 $\mu\text{g}/\text{m}^2$), MCPA (6.2-15 $\mu\text{g}/\text{m}^2$) and terbutylazin (2.1-6.5 $\mu\text{g}/\text{m}^2$). Isoproturon, atrazine and lindane were found despite the fact that they are not used in Denmark. The deposition of these substances is thought to take place after long-range transport. The measured concentrations for all substances were below the 0.1 $\mu\text{g}/\text{l}$ EU drinking water limit, concentrations were averaged for two months.

A screening study was also performed in Denmark in 2000-2001 (Asman et al., 2005). 80 substances were analysed in precipitation collected at two locations, 57 of the substances were detected. Ten of the substances were not registered for use in Denmark and the authors conclude that these must have been transported in the atmosphere at least 60-80 km. Pendimethalin and a degradation product of terbutylazine were the two most frequently detected substances.

Hermanson et al. (2005) found that vapour pressure is a property that affects the pesticides tendency to move into the air. They also comment that a high water solubility dose not seem to prevent the pesticide from entering the atmosphere if the vapour pressure is high. Guth et al. (2004) also investigated the properties of pesticides versus their volatilisation. Vapour pressure was the single best property explaining losses from vegetation and soil. There is generally no volatilisation if the vapour pressure is less than 10^{-3} Pa for soil and 10^{-4} Pa for vegetation. The authors suggest that vapour pressure can be used to predict volatilisation. The Henry's law constant was shown to have some influence on volatilisation from soil but not from vegetation. Other mentioned properties were water-air partitioning coefficient and soil-air partitioning coefficient.

In this report we summarize results from the ongoing national monitoring programme of pesticides in atmospheric deposition. The objective has been to investigate the presence of some currently used pesticides, as well as some banned pesticides, in precipitation and to calculate the deposition loading in Sweden. Occurrence of non-registered pesticides in rainfall over Sweden indicate medium- to long-range transport and was evaluated using back-trajectory analyses to correlate monitoring results with the prevailing wind direction during the same period. Finally suggestions are made on how to enhance the monitoring programme in the future to increase our knowledge on the extent of pesticide deposition in Sweden and further explore long-range transport of also currently used pesticides.

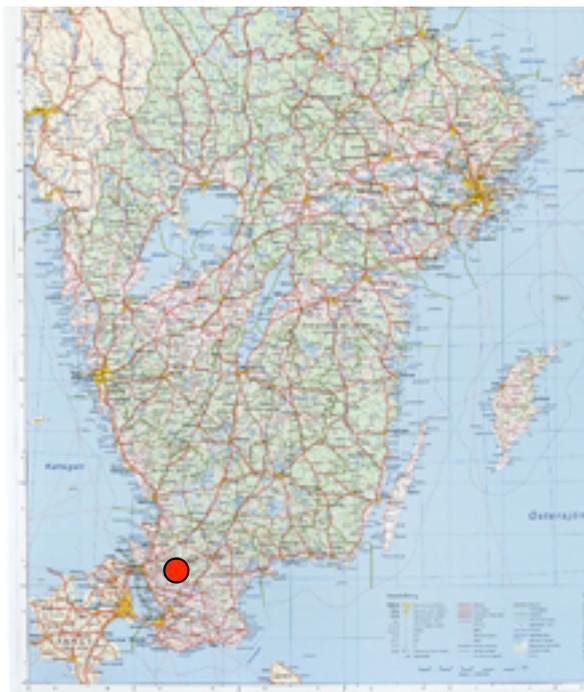


Figure 1. Location of Vavihill monitoring site in southern Sweden (red dot) (EMEP measuring station SE11).



Figure 2. Bulk sampler with a stainless steel funnel mounted on a refrigerator containing the sampling bottle.

Material and methods

Sampling site

Rainwater was collected at Vavihill in the very south of Sweden (Figure 1). Vavihill (56°01'N, 13°09'E) is a rural background site where other measurements on atmospheric chemistry and deposition (though not pesticides) are performed within the European Monitoring and Evaluation Programme (EMEP, station no SE11). It is situated away from the agricultural areas, in a sheltered forest, to avoid direct wind-drift of pesticides. Rainfall was registered, on a daily basis, ca 500 m from the monitoring site, except during 2002 when it was retrieved from an official weather station (Klippan) ca 12 km north of Vavihill.

Sampling methodology

Rainwater was collected using a bulk sampler, consisting of a 0.5-m² funnel of polished stainless steel placed over a refrigerator (Figure 2). During the sampling period rainwater was stored in a 10-l glass bottle inside the refrigerator at 4°C. Sampling was event-driven, with the rainwater transferred to the laboratory after significant rain events or when more than 10-20 mm of rain had accumulated. The maximum length between the onset of rainfall and the sampling occasion was 14 days. Event-related sampling was used to *i*) ensure that enough water was collected for the analytical procedure that requires a minimum of ca 5 l of rainwater and *ii*) facilitate the use of back-trajectory analysis when evaluating the results to correlate these with the prevailing wind during the collection period.

On each sampling occasion the total volume of rainwater collected was transferred to 2.5-l bottles for immediate transport to the laboratory at SLU in Uppsala. To keep the samples refrigerated during transport ice packs were placed in the shipping boxes. Before starting a new sampling period the funnel and the 10-l glass bottle were thoroughly washed with ethanol and distilled water. Blank samples, running distilled water through the equipment after the rinsing procedure, were occasionally collected. No traces of pesticides were detected on any occasion demonstrating that the cleaning procedure was adequate.

Sampling was carried out during the main season for pesticide application in Sweden, i.e. during May-June and September-October, resulting in 10-13 samples being collected each year (Table 1). The sampling season was kept as constant as possible, but the number and distribution of rain events, together with a fixed number of samples included in the monitoring programme, decided the exact time frame.

Analytical procedures

The pesticide laboratory at the Department of Environmental Assessment, SLU, Uppsala performed the analysis of pesticides residues in rainwater. The laboratory is accredited by SWEDAC (Swedish Board for Accreditation and Conformity Assessment) for pesticide analyses.

A total of 90 substances were included in the analyses during one or several years, 76 of these being included during all four years (Appendix 1). In total, 38 herbicides, 16 fungicides, 24 insecticides and 12 metabolites were analysed. Pesticides were primarily chosen based on the selection made for the monitoring programme for surface and ground waters in Sweden,

representing the most commonly used pesticides in Sweden (except glyphosate and sulfonylurea herbicides), as well as pesticides listed in Appendix 10 of the Water Framework Directive. A majority of pesticides listed in Appendix 10 are not registered for use within Sweden, in addition to these some other pesticides no longer registered in Sweden, or the EU, were included (e.g., aldrin, chlordane- γ , 2,4-D, DDT, dichlobenil, diclofol, heptachlor and vinclozolin). All together a total of 22 compounds (together with some of their metabolites) included in the monitoring programme are not used within Sweden (Appendix 2) and some of the other pesticides have only limited use in Sweden, e.g. chlorpheninfos and chlorpyrifos.

The analyses were performed on unfiltered rainwater samples and involved two different methods, one for phenoxy acids and similar polar compounds (OMK 50:8) using solid phase extraction and one for semi-polar and neutral compounds (OMK 51:5) using liquid/liquid extraction. Large volumes of water were extracted (1.5 l with OMK 50:8 and 3 l with OMK 51:5) and both methods involved quantification with GC-MS. All detects were confirmed using two masses with a general limit of detection (LOD) in the range of 0.001-0.01 $\mu\text{g/l}$ (Appendix 1). Quality assurance procedures included field blanks and laboratory blanks. For each batch of analyses a recovery test was performed with a number of the compounds most frequently detected. Surrogate and internal standard were added to both methods. The limit of quantification (LOQ) was generally 2-5 times higher than the LOD. Positive detects between LOD and LOQ were reported as trace concentrations and were included in the calculation of deposition using the average value between LOD and LOQ.

Results

Between 30 and 40 substances were detected each year (Table 1), with a maximum of 29 substances in a single sample. The most intense application period for pesticides is during spring and early summer each year and accordingly the highest number of substances in rainfall was detected in May during all years. On a whole, lowest concentrations were detected during 2004 sampling season, both for single compounds (maximum 0.08 $\mu\text{g/l}$) and as a total concentration (maximum 0.24 $\mu\text{g/l}$). In 2005 elevated concentrations occurred, particularly for prosulfocarb detected during autumn at a maximum concentration of 0.8 $\mu\text{g/l}$.

The total concentration of pesticides in a single sample varied from trace levels (i.e. below the LOQ) up to 0.92 $\mu\text{g/l}$ in a sample from September 2005. Generally, 2003 and 2005 were years with higher concentrations and 2002 and 2004 were years with lower concentrations. During the first three years of sampling higher concentrations were found in spring than in autumn, but in 2005 the opposite could be noticed with several samples from October having relatively high concentrations. During all years samples were retrieved during May with a total concentrations above 0.2 $\mu\text{g/l}$. During the end of June and early autumn the concentrations decreased to rise again in October.

The years of 2003 and 2005 had higher calculated seasonal deposition than the other two years, following the pattern of concentrations. For example all substance but one were deposited in larger amounts in 2003 than in 2002. Prosulfocarb was the substance with the highest deposition in three of four years (Appendix 3).

A total of 47 substances were detected on one or several occasions during the four years, 26 of these being herbicides, 8 fungicides, 8 insecticides and 5 metabolites (Table 2). Summarising data from all four years 28 substances were found in more than 20% of the

Table 1. Summary data of rainwater monitoring in Sweden at Vavihill during 2002-2005

	2002	2003	2004	2005
Number of samples	10	12	12	13
Sampling period	May-Jun, Sep-Oct	Apr-Jun, Sep-Nov	May-Jul, Sep-Oct	May-Jun, Sep-Oct
Total rainfall during sampling period (mm)	178	255	371	318
Number of analysed substances	79	81	85	86
Number of detected substances	31	36	34	38
Max. conc., single substance ($\mu\text{g/l}$)	0.3 (Pros)	0.4 (IPU)	0.08 (Fen)	0.8 (Pros)
Max. total conc. in a sample ($\mu\text{g/l}$)	0.37 (Oct)	0.59 (May)	0.24 (May)	0.92 (Sep)
Max. number of substances per sample	22 (May)	27 (May)	20 (May)	29 (May)
No of detected substances not registered for use in Sweden, metabolites in brackets	8 (+3)	11 (+4)	9 (+3)	11 (+2)
Max. deposition, single substance ($\mu\text{g/m}^2\cdot\text{season}$)	6.6 (Pros)	25.4 (IPU)	5.4 (Pros)	43.4 (Pros)
Calculated tot seasonal deposition (mg/ha)	279	873	419	978

Pros = prosulfocarb; IPU = isoproturon; Fen = fenpropimorph.

samples (Figure 3). Twelve of these substances are not registered for use in Sweden (red bars in Figure 3).

Twenty-five substances were detected all four years, most of them herbicides but also some fungicides. MCPA is an herbicide that is sold in large quantities in Sweden, ca 200 tonnes/year, only glyphosate is sold in larger quantities (Kemikalieinspektionen, 2005). MCPA was also frequently found in precipitation, on average in ca 80% of the samples during the four year period (Figure 3) ranging from 67-100% of the samples during single years (Table 2). Fenpropimorph, ethofumesate, prosulfocarb and isoproturon were other substances, registered for use in Sweden, with a high frequency of detection. The sold amounts of fenpropimorph has increased from 20 to 45 tonnes per year since the start of the precipitation monitoring in 2002 (Kemikalieinspektionen, 2005). Ethofumesate is sold in amounts of a few tonnes per year and prosulfocarb in ca. 10 tonnes/year, so the frequent detections are not explained with a high use in Sweden. Isoproturon on the other hand is sold in large quantities, ca 75 tonnes/year, and is also one of the more widely used herbicides in cereal growing regions throughout Europe.

Of those 25 substances detected during all four years, eight of these were not used in Sweden and therefore likely originating from other parts of Europe. On a whole, 18 of the detected substances were not used in Sweden during the year of sampling. Lindane and HCH-alpha (a by-product in lindane production) have not been used in Sweden since 1989 and their detection limits have not changed dramatically during the sampling period. Lindane was the most frequently detected substance in this study (Figure 3). During the first three years lindane was detected in all but one sample (Table 2). In 2005 the detection frequency was lower, all samples of lindane 2004-2005 were below the limit of quantification. HCH-alpha had a total detection frequency of just below 50%. The detection frequency was 100% in 2002, but it was not found at all in 2005 (Table 2), which indicates a decreasing use since the beginning of the measurements, in response to the recent ban of lindane within Europe (compare the Discussion section).

Terbutylazin was banned for use in Sweden in 2003 although it had not been sold since 1999. It was the third most frequently detected substance and its metabolite DETA was the fourth most frequently detected. No decline in detection frequency can be seen for any of the two (Table 2). Vinclozolin was found more frequently in the second half of the programme than in the first, this might be due to a lowered detection limit. Diuron and dichlobenil were also detected more frequently during the second part of the measurements. 2,4-D and atrazine seem to have the opposite trend with a decreasing detection frequency during since the start of the programme.

Five substances were detected in all samples at least one of the years; these were MCPA (2005), lindane (2002 and 2004), HCH-alpha (2002), chlorpyrifos (2005) and endosulfan-beta (2005). For the last two ones the limit of detection was lowered during the study period. Three substances were detected in concentrations above 0.1 µg/l; MCPA twice, prosulfocarb three times and pendimetalin once (Table 2).

Ten substances were only found in one of the years and most of them only occasionally. Three substances were found very frequently during a single year (esfenvalerate, chlorpyrifos and lambda-cyhalothrin, all insecticides). This may be explained by the fact that the detection limit was lowered one order of magnitude for these substances this particular year (Table 2 &

Table 2. Detection frequency and maximum concentrations for substances found in precipitation at Vavihill during 2002-2005

Substance	Detection frequency				Maximum concentration (µg/l)			
	2002	2003	2004	2005	2002	2003	2004	2005
aclonifen (H)	10%	33%	33%	46%	t	0.01	0.01	0.014
alachlor* (H)		17%				0.01		
atrazine* (H)	60%	58%	33%	31%	0.03	0.02	0.01	0.014
DIPA (M)		8%				t		
azoxystrobin (F)	50%	33%	17%	46%	0.02	t	t	0.013
bentazone (H)	50%	25%	33%	38%	0.01	0.01	0.005	0.014
bitertanol (F)		17%	8%			t	0.04	
chloridazon (H)				15%				0.02
chlorpyrifos (I)				100%				t
clopyralid (H)	20%	25%	17%	15%	0.01	0.02	t	t
cyprodinil (F)	-	-	-	62%	-	-	-	0.01
2,4-D* (H)	50%	67%	17%	38%	0.02	0.02	0.008	0.031
DDT-p,p* (I)		8%				t		
dicamba (H)	40%	42%	17%	31%	0.01	0.02	0.004	0.017
dichlobenil* (H)	50%	42%	17%	85%	t	0.008	t	t
BAM* (M)		8%				t		
dichlorprop (H)	40%	33%	25%	23%	0.01	0.03	0.008	0.014
diflufenican (H)	10%	58%	8%	31%	t	0.02	0.003	0.015
diuron* (H)	20%	42%	42%	62%	t	0.008	t	0.01
α-endosulfan* (I)		17%	8%	85%		t	t	t
β-endosulfan* (I)			17%	100%			t	0.001
endosulfan-sulfate (M)	10%		8%	38%	t		t	t
esfenvalerate (I)				46%				t
ethofumesate (H)	60%	58%	25%	62%	0.02	0.03	0.03	0.01
fenpropimorph (F)	60%	42%	58%	54%	0.06	0.06	0.07	0.012
fluroxypyr (H)	50%	33%	42%	46%	0.01	0.02	0.02	0.016
iprodione (F)	20%			8%	0.03			t
isoproturon (H)	20%	75%	33%	62%	0.07	0.06	0.04	0.05
lambda-cyhalothrin (I)				38%				t
lindane (γ-HCH)* (I)	100%	92%	100%	62%	0.002	0.008	t	t
α-HCH (M)	100%	83%	17%		t	t	t	
MCPA (H)	70%	67%	75%	100%	0.03	0.15	0.05	0.21
mecoprop (H)	40%	67%	25%	46%	0.008	0.02	0.006	0.013
metamitron (H)		8%	8%	-		0.01	t	-
metazachlor (H)	10%	42%	42%	31%	t	0.03	0.02	0.069
pendimethalin (H)	10%	25%	17%	31%	t	0.05	0.01	0.2
pirimicarb (I)	30%		25%		t		t	
propiconazole (F)	30%	33%	33%	54%	t	0.01	t	0.012
propyzamide (H)		8%				t		
prosulfocarb (H)	40%	42%	58%	62%	0.3	0.4	0.05	0.8
quinmerac (H)			8%	15%			t	0.022
simazine* (H)	10%			8%	t			t
terbuthylazine* (H)	50%	58%	58%	62%	0.02	0.03	0.04	0.061
DETA (M)	40%	67%	50%	62%	0.04	0.07	0.04	0.078
tolyfluanid (F)	30%	8%	25%	8%	t	t	t	t
trifluralin* (H)		17%		8%		t		t
vinclozolin* (F)	40%	17%	75%	62%	t	0.02	t	t

H = Herbicide, F = Fungicide, I = Insecticide, M = Metabolite.

* = pesticide not registered for use in Sweden.

t = trace (concentration between LOD and LOQ).

- = not analysed.

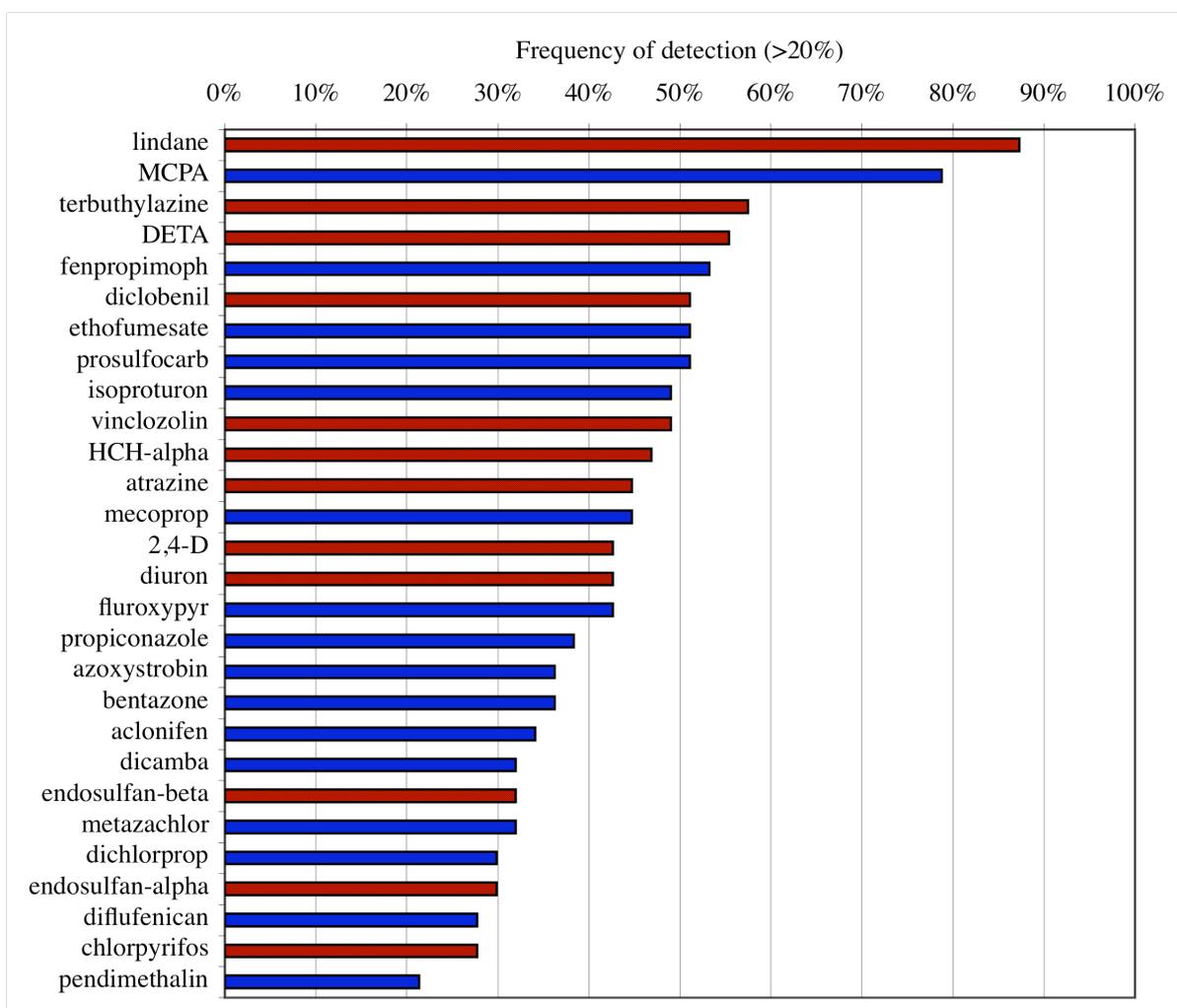


Figure 3. Detection frequency for substances detected in more than 20% of the samples. Red coloured bars indicate that the substance is not registered for use in Sweden.

Appendix 1), but a particular high pressure from insect pests that year may also be part of the explanation.

The figure with average seasonal deposition (Figure 4) gives a slightly different picture than Figure 3, with detection frequencies. The highest average deposition rate was calculated for prosulfocarb, which was found in 50% of the samples. Isoproturon had the second highest deposition rate and also had a deposition frequency of 50%. Compared to MCPA (third highest deposition rate), isoproturon was found in fewer samples but at higher concentrations. Isoproturon was detected in a few samples in early spring but mainly in the autumn while MCPA was detected mostly in the spring season and only occasionally and at low concentrations during autumn. This corresponds well with the main application seasons for these two herbicides.

Terbutylazine and DETA have the third highest deposition rate if put together. Both substances were also detected frequently. In contrast, metazachlor and pendimethalin have a

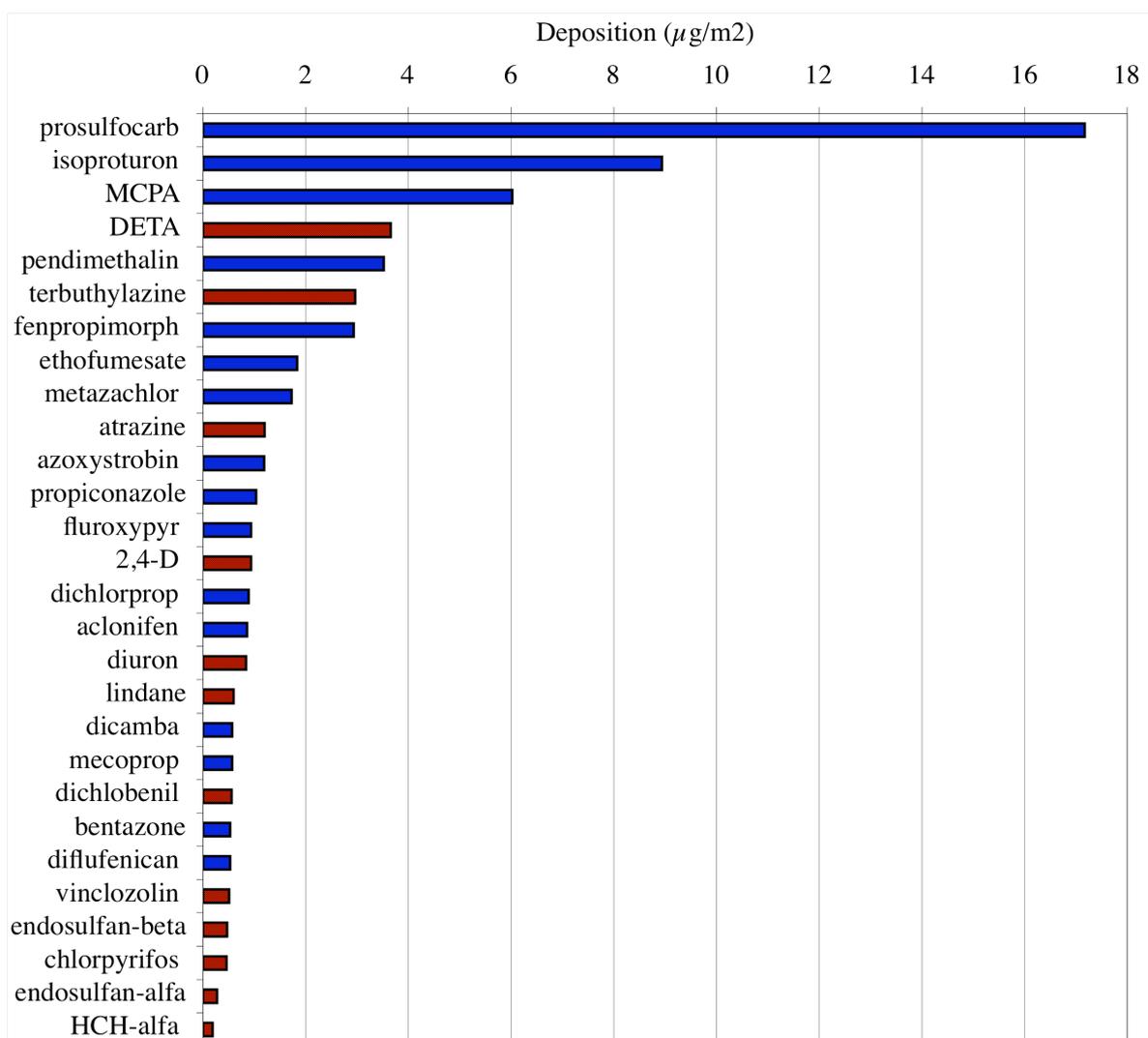


Figure 4. Average seasonal deposition of individual compounds at Vavihill 2002-2005. Substances detected in more than 20% of the samples are included. Red coloured bars indicate that the substance is not registered for use in Sweden.

rather high deposition rate, despite not being detected very frequently. They were also mostly found in the autumn and only rarely in spring, reflecting that the main application season for these compounds is during the autumn. Dichlobenil, lindane, HCH-alpha and vinclozolin, on the other hand, were found regularly, but their calculated deposition rate was relatively low. These substances were only detected at low concentrations, possibly indicating a longer residence time in the atmosphere for these substances before being deposited at Vavihill.

Results compared to literature

The high number of substances not registered for use in Sweden that were frequently detected indicate that there is a medium- to long-range transport of several substances. A high detection frequency of lindane is commonly reported from Europe and it agrees with the

results of this study. HCH-alpha has too been frequently reported in other investigations throughout Europe. Furthermore, atrazine has been found in other studies to be transported over long distances, as was the case in this study. All measured concentrations in this study were below one microgram per litre, which is in good agreement with the results of others.

In the Danish study (Ellerman et al., 2005) pendimetalin was found to give the highest contribution to deposition in Denmark. In this study it was the fifth most contributing substance to deposition in southern Sweden. MCPA and terbuthylazine and its metabolite DETA were frequently found in both countries. Terbuthylazine is still used in Denmark. Deposition amounts were in the same range for several substances although the Danish values were calculated for 20 substances and a whole year, while in this investigation values were derived only for a few months each year, but including more substances. The sampling season was targeted to the main application season in Sweden, i.e. assuming the major part of the deposition to occur as a result of local sources. However, the spraying season starts earlier and ends later further south and therefore it might be expected that deposition of pesticides also takes place at other times of the year than included in this study due to a longer spraying season than in Sweden.

The Danish study did not find any substance above 0.1 µg/l, i.e. the EU maximum permissible concentration in drinking water. Results from this study found four substances occasionally exceeded that limit. The lower concentrations in the Danish investigation can most likely be explained by the fact that the sampling period in that study lasted for two months, resulting in the samples being more diluted and possibly also some of the pesticides being subjected to degradation.

HCH and trazines were the most commonly detected substances in southern Sweden during the early 1990's (Kreuger & Staffas, 1999). Lindane was still the most frequently found substance in this investigation, but the metabolite alpha-HCH has decreased. This may reflect that few countries in Europe have used technical grade HCHs, in which HCH-alpha is the dominant isotope, since the early 1980s, but lindane (pure HCH-gamma) was used until the late 1990s (Li, 1999). 2,4-D and atrazine were found in 50 % of the samples in the previous Swedish study and in the present, the detection frequency was 43-45%.

In contrast to Dubus (et al. 2003) we found that substances that must have been subject to medium- and long-range transport because they are not used in Sweden can still show seasonal variation such that the concentrations are higher during the application season in Continental Europe. The conclusion of Dubus and co-workers is probably more related to persistent substances like lindane and many studies of pesticide deposition is based on that particular substance. Transport over longer distances will also have the effect of levelling out the concentration over the year.

An interesting new development is the finding of what has been regarded as easily degraded pesticides, e.g., malathion, in glacier ice in the Arctic (Hermanson et al., 2005). Other previous publications also report on currently-used pesticides that have undergone long-range transport (Chernyak et al., 1996; Rice & Chernyak, 1997). Particularly high concentrations with possible ecotoxic effects have been found in brine inside the sea ice in the Arctic (Kylin unpublished results). These results show the necessity to further investigate the long-range transport of currently-used pesticides.

Table 3. Pesticides detected at concentrations exceeding Swedish target values for surface waters during 2002-2005 at Vavihill

Substance	Target value ($\mu\text{g/l}$)	Max. conc. ($\mu\text{g/l}$)	Times \geq target value
fenpropimorph	0.02	0.08	9
terbuthylazine	0.02	0.06	8
esfenvalerate	0.0001	0.005	6
isoproturon	0.3	0.4	2
pendimethalin	0.1	0.2	1

Discussion

There are no target values, or maximum permissible amounts/concentrations, for pesticides in atmospheric deposition. During the registration procedure a number of toxicological evaluations are carried out to protect terrestrial and aquatic species in the near-by area, e.g. due to wind-drift. Based on the results in this report it can be calculated that the deposited amounts roughly correspond to ca 0.01-0.0004% of the applied dose, which likely is below what could be expected in the vicinity of a treated field. However, the species included in the standard tests for toxicity evaluation during the registration procedure are probably not representative of those living in areas away from the main agricultural regions or in pristine remote areas. Information on possible effects from diffuse pollution on non-target species of low concentrations of currently used pesticides in the atmosphere have so far received little attention in the scientific literature.

Comparing the concentrations detected in rainfall in this study with the preliminary Swedish target values to protect surface water quality (set by the Swedish Chemicals Inspectorate, KemI) shows that some of the pesticides occasionally exceeded these values (Table 3). The fungicide fenpropimorph, with a relatively high vapour pressure (compare Appendix 4) and a target value of 0.02 $\mu\text{g/l}$, was detected the most frequently at levels close to or above this concentration in rainfall from the Vavihill monitoring site.

Calculations show that a substantial part of the total deposition load is from pesticides no longer registered for use in Sweden. In 2002 restricted pesticides constituted 21% of the total seasonal load, corresponding figure in 2003 was 20%, in 2004 25% and in 2005 15%. As a whole, during the four-year period on average 20% of the pesticide load originated from pesticides applied outside of Sweden indicating a substantial contribution from transboundary atmospheric transport. Possibly, also some pesticides, though registered for use in Sweden, originated from other countries. For example, a simple correlation analysis between the amount of pesticides deposited at Vavihill and the amounts sold in Sweden and Denmark, respectively, demonstrate a better correlation between the deposition at Vavihill and the Danish sales figures ($R^2 = 0.46$) than with the Swedish sales figures ($R^2 = 0.39$) (Figure 5). For example the herbicide prosulfocarb, that was one of the compounds having the highest deposition rate during all years has a quite limited use in Sweden (ca 10-15 tonnes/year), whereas sales figures in Denmark are much higher (ca 400-500 tonnes/year).

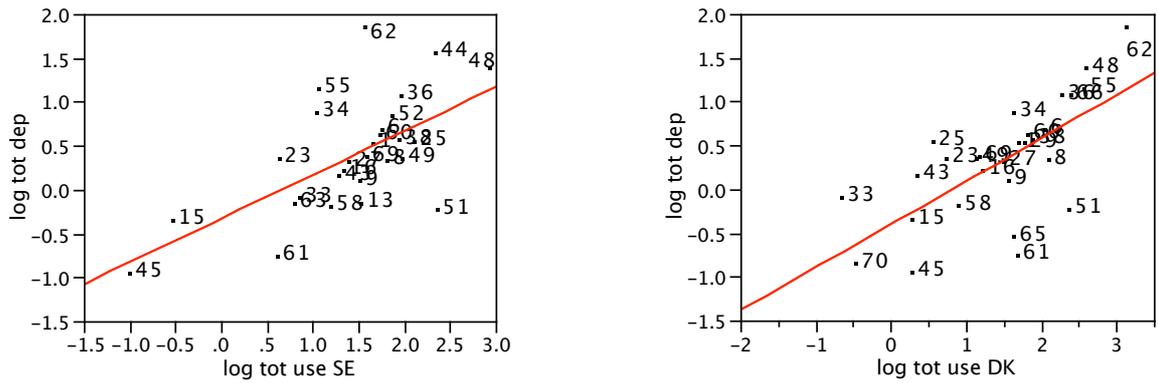


Figure 5. Correlation between total deposition at Vavihill during 2002-2005 and the sum of sold amounts of currently used pesticides in Sweden (to the left, $R^2 = 0.39$) and Denmark (to the right, $R^2 = 0.46$) during 2002-2004.

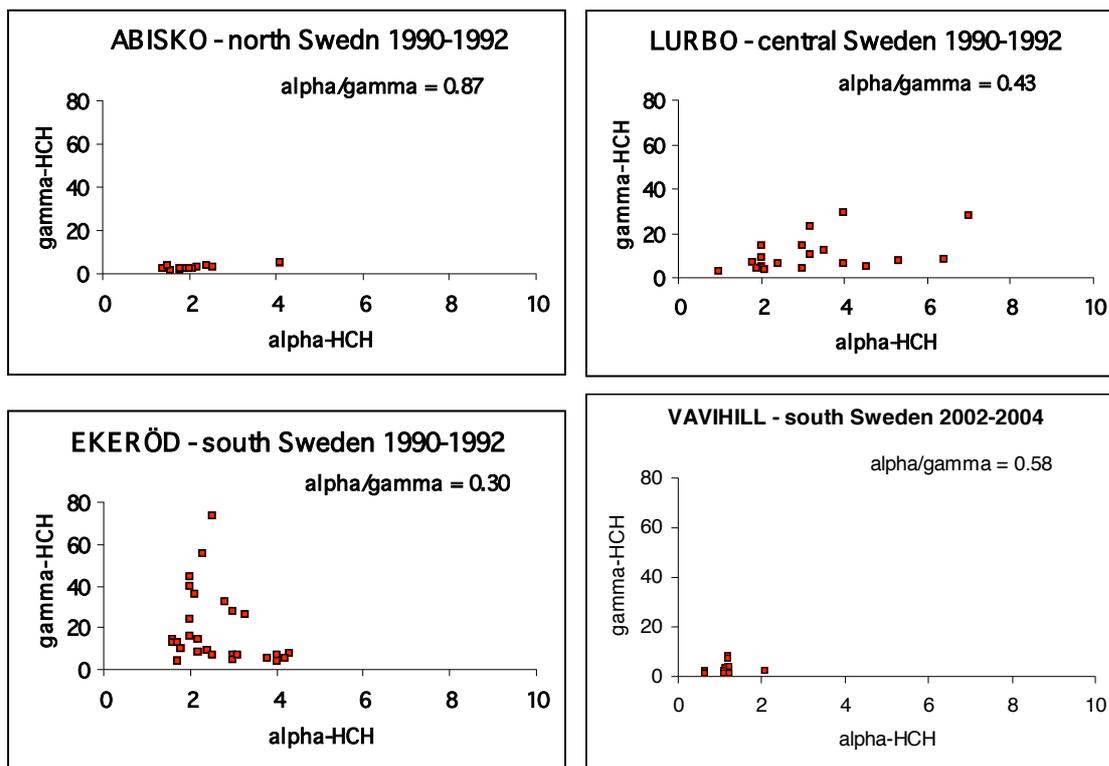


Figure 6. Lindane (gamma-HCH) vs alpha-HCH concentrations (ng/l) in Swedish rainwater during the early 1990's from three different sites along a south-north gradient and at Vavihill in the south of Sweden during the 2000's .

Lindane was found at decreasing concentrations during 2002-2005 at Vavihill, reflecting the recent ban of lindane within Europe. Findings of lindane during 2005 were lower than the other years, with measurable concentrations only when the prevailing winds came from Continental Europe, the previous years lindane was detected regardless of wind direction.

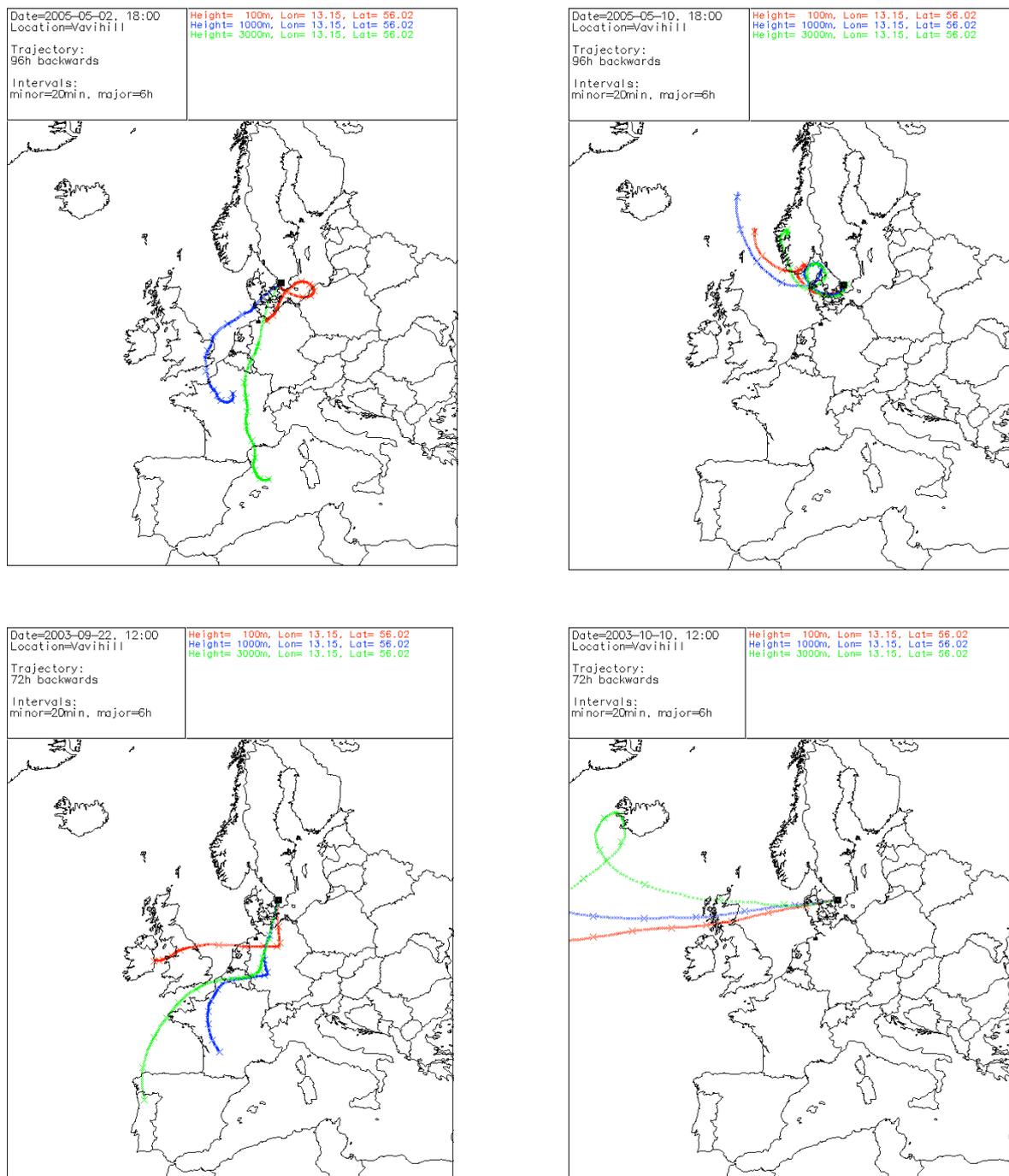


Figure 7. Back-trajectory calculations showing prevailing wind-directions during two major rain events during spring (top figures) and autumn seasons (bottom figures) at Vavihill.

Also, in 2005, for the first time, no traces of alpha-HCH were detected. Concentrations of lindane (gamma-HCH) has decreased considerably since the early 1990's with an alpha/gamma-ratio today being close to the levels previously detected at Abisko in the far north of Sweden (Figure 6), indicating a longer atmospheric residence time for lindane deposited in southern Sweden today.

In order to explore the origin of air masses during rain events collected at the Vavihill site back-trajectory analyses was performed. In Figure 7 a few examples are presented. During spring 2005 a major rainfall occurred on 2 May when air masses came from the south-west (Figure 7, top left figure). A large number of pesticides was detected, 25 pesticides and 3 metabolites, with 9 of the pesticides not being registered in Sweden. The following week a major rain event occurred on 10 May when air masses came from the north-west (Figure 7, top right figure). Fewer pesticides were detected, 15 pesticides and 2 metabolites, with 4 of the pesticides not used in Sweden. On this occasion no traces of the otherwise frequently detected pesticides atrazine, 2,4-D, lindane and vinclozolin were found in the deposition.

During autumn 2003 a major rainfall occurred on 22 September when air-masses came from the south-west (Figure 7, bottom left figure). Total deposition included 11 pesticides and two metabolites, with 6 of the pesticides not being registered in Sweden. A few weeks later a major rain event occurred on 10 October when air-masses came from the west-northwest (Figure 7, bottom right figure). Also on this occasion fewer pesticides were detected, 5 pesticides and two metabolites, with only one of the pesticides and the two metabolites not being used in Sweden.

Suggestions for future work

The results so far are interesting, but far from conclusive in describing the total deposition pattern of currently used pesticides in Sweden. Firstly, the basis for selecting the pesticides was mainly those compounds that were easily included, i.e., compounds that were already included in the Swedish environmental monitoring programme for surface and ground water. This leaves out several possible compounds that may reach Sweden from other countries. Secondly, there is only one sampling station. Sampling stations continuously operating in other parts of Sweden or Scandinavia would give better background information on the actual deposition pattern and more information on the possible source areas and transport routes. Thirdly, this programme only covers wet deposition. A programme that also included air (gas and particle phase) sampling and dry deposition would give information on transport mechanisms.

There is an increasing mass of findings of compounds in the high Arctic (e.g. Chernyak et al., 1996; Rice & Chernyak, 1997; Hermanson et al., 2005; Kylin unpublished data), indicating that our understanding of the actual longevity of many currently-used pesticides in air is poor, and that these are longer than the current estimates. One obvious candidate to include in the monitoring programme is dachthal (tetrachloro-dimethylterephthalate), a herbicide. Although dachthal contains two ester groups that on paper seems to be easily degradable it is found in every water sample from the high arctic that we have so far looked at (Kylin, Jantunen & Bidleman, unpublished; Muir, unpublished).

The Arctic Monitoring and Assessment Programme expert meeting on persistent organic pollutants in Burlington, Ontario, Canada, 6-8 March 2006, commissioned a report on currently used pesticides (Hermanson & Kylin, *in prep*). The future understanding of why we find currently used pesticides in very remote areas, such as the Arctic, would benefit greatly from more sampling stations for these compounds at lower latitudes, stations that should include a broad spectrum of sampling techniques, not only wet deposition. Sampling should also be made more frequently than today's programme can accommodate.

Results from different investigations show that there is significant contribution to large areas from modern agricultural pesticides via atmospheric deposition. Results presented in this report contain the only reported measurements of currently used pesticides from Sweden since the early 1990's. Part of the deposited load is due to long-range transboundary deposition.

Consequently, it is essential to collect more data from other parts of Sweden and also extend the sampling periods. This would give additional opportunity to study long-range transport of pesticides, since the application season starts much earlier, and ends later in countries further south.

To sum up our recommendations for future work:

* Additional monitoring sites

A single monitoring site presents uncertainties in the actual deposition loads and of how representative they are for larger regions, including a south-north gradient.

* A longer sampling season

The current monitoring program is limited to a four-month period. However, the application season starts earlier and ends later in Continental Europe than in Sweden, including many volatile fungicides and insecticides being applied during the summer months, e.g. in fruit orchards and wines, when no collection of deposition is done in the current programme. It would also be beneficial for the interpretations if more samples could be taken and with a higher frequency.

* Inclusion of additional pesticides

To select additional pesticides based on their intrinsic properties (mainly vapour pressure, half-life in air and persistence) and used amounts in Europe (the review also suggesting pesticides that could be excluded from the analytical list). There are some 400 different pesticides applied throughout Europe. The least investigated environmental fate processes today is atmospheric transport. Little is known of atmospheric half-lives and degradation processes in the air.

* Air sampling

A programme that also include air (gas and particle phase) sampling and dry deposition would give information on transport mechanisms.

Abbreviations

BAM = 2,6-diklorobenzamide, a metabolite to the herbicide dichlobenil.

DEA = deetylatriazine, a metabolite to the herbicide atrazine.

DIPA = deisopropylatriazine, a metabolite from the herbicide atrazine.

DETA = deetylterbuthylazine, a metabolite to the herbicide terbuthylazine.

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Appendices

Appendix 1. Substances included in the analysis and their limit of detection (median value) during 2002-2005. Metabolites are listed with their mother substance

Substance	Limit of detection (µg/l)			
	2002	2003	2004	2005
acлонifen (H)	0.01	0.002	0.002	0.001
alachlor (H)	0.002	0.005	0.006	0.006
aldrin (I)	0.001	0.001	0.003	0.0004
alpha-cypermethrin (I)	0.01	0.003	0.002	0.0002
atrazine (H)	0.002	0.002	0.002	0.003
DEA (M)	0.003	0.005	0.001	0.003
DIPA (M)	0.02	0.02	0.04	0.02
azoxystrobin (F)	0.004	0.005	0.01	0.004
benazolin (H)	-	0.002	0.001	0.001
bentazone (H)	0.002	0.002	0.001	0.001
beta-cyfluthrin (I)	-	-	-	0.0002
bitertanol (F)	0.01	0.013	0.02	0.005
carbofuran (I, M)	0.005	0.005	0.006	0.01
carbosulfan (I)	0.003	0.003	0.002	-
carfentrazone-ethyl (H)	-	-	0.005	-
chlordane-γ (I)	0.001	0.0006	0.0002	0.0007
chlorfenvinphos (I)	0.005	0.003	0.0004	0.0001
chloridazon (H)	0.02	0.006	0.006	0.005
chlorpyrifos (I)	0.002	0.002	0.0002	0.00003
cinidon-ethyl (H)	-	-	0.01	-
clopyralid (H)	0.004	0.003	0.003	0.005
cyanazine (H)	0.009	0.004	0.004	0.005
cyfluthrin (I)	0.02	0.005	0.004	0.0002
cypermethrin (I)	0.01	0.005	0.004	0.0004
cyprodinil (F)	-	-	-	0.002
2,4-D (H)	0.002	0.001	0.002	0.001
DDT-p,p (I)	0.001	0.001	0.002	0.0006
DDD-p,p (M)	0.0005	0.001	0.001	0.002
DDE-p,p (M)	0.002	0.001	0.001	0.0008
DDT-o,p (M)	0.001	0.001	0.001	0.002
deltamethrin (I)	0.005	0.004	0.002	0.0004
dicamba (H)	0.002	0.001	0.001	0.001
dichlobenil (H)	0.0007	0.002	0.002	0.001
BAM (M)	0.01	0.004	0.002	0.003
dichlorprop (H)	0.002	0.001	0.001	0.001
dicofol (I)	-	0.01	0.01	0.0006
diflufenican (H)	0.002	0.001	0.001	0.003
dimethoate (I)	0.03	0.01	0.01	0.01
diuron (H)	0.001	0.001	0.001	0.001
α-endosulfan (I)	0.006	0.002	0.001	0.0001
β-endosulfan (I)	0.007	0.002	0.001	0.00004
endosulfan-sulfate (M)	0.003	0.002	0.001	0.0002
esfenvalerate (I)	0.005	0.004	0.001	0.0001
ethofumesate (H)	0.003	0.002	0.003	0.002
fenitrothion (I)	-	-	-	0.005
fenoxaprop-P (H)	0.004	0.002	0.002	0.002
fenpropimorph (F)	0.002	0.002	0.002	0.003
flamprop (H)	0.003	0.002	0.001	0.001
fluroxypyr (H)	0.003	0.004	0.002	0.002
flurtamone (H)	-	-	0.01	0.007

Substance	Limit of detection (µg/l)			
	2002	2003	2004	2005
fuberidazole (F)	-	-	-	0.002
heptachlor (I)	0.002	0.003	0.002	0.0008
heptachlor epoxide (M)	0.002	0.001	0.004	0.004
hexachlorobenzene (F, M)	0.0004	0.0005	0.0002	0.0004
hexazinone (H)	0.005	0.005	0.005	0.005
imazalil (F)	0.03	0.008	0.01	0.009
imidaclopride (I)	-	-	-	0.02
iprodione (F)	0.005	0.005	0.005	0.005
isoproturon (H)	0.002	0.002	0.002	0.001
lambda-cyhalothrin (I)	0.002	0.005	0.001	0.00006
lindane (γ-HCH) (I)	0.0003	0.0003	0.0002	0.0006
α-HCH (M)	0.0003	0.0003	0.0002	0.0004
β-HCH (M)	0.0005	0.0005	0.0006	0.0003
δ-HCH (M)	0.0003	0.0003	0.0003	0.0002
MCPA (H)	0.002	0.001	0.001	0.001
mecoprop (H)	0.002	0.001	0.001	0.001
metalaxyl (F)	0.001	0.005	0.004	0.006
metamitron (H)	0.01	0.009	0.01	-
metazachlor (H)	0.004	0.002	0.004	0.003
methabenzthiazuron (H)	0.03	0.02	0.02	0.01
metribuzin (H)	0.01	0.005	0.004	0.006
penconazole (F)	-	-	-	0.002
pendimethalin (H)	0.005	0.007	0.004	0.004
permethrin (I)	0.02	0.008	0.01	0.002
phenmedipham (H)	0.07	0.08	0.03	0.03
pirimicarb (I)	0.002	0.003	0.002	0.002
prochloraz (F)	0.005	0.005	0.05	0.009
propiconazole (F)	0.008	0.005	0.01	0.003
propyzamide (H)	0.01	0.006	0.004	0.004
prosulfocarb (H)	0.003	0.005	0.003	0.004
pyraclostrobin (F)	-	-	0.05	0.02
quinmerac (H)	0.003	0.002	0.002	0.001
simazine (H)	0.01	0.005	0.003	0.003
terbutryn (H)	0.003	0.002	0.005	0.005
terbuthylazine (H)	0.0007	0.001	0.001	0.002
DETA (M)	0.005	0.001	0.001	0.001
tolclofos-methyl (F)	0.002	0.002	0.002	0.002
tolyfluanid (F)	0.005	0.005	0.005	0.003
trifluralin (H)	0.001	0.001	0.001	0.0008
vinclozolin (F)	0.001	0.003	0.0002	0.0001

H = Herbicide, F = Fungicide, I = Insecticide, M = Metabolite

BAM = 2,6-Dichlorbenzamid

DEA = Deethylatrazine

DIPA = Deisopropylatrazine

DETA = Deethylterbuthylazine

Appendix 2. Substances included in the analyses including information on registration status (during 2004) and analytical method used

Substance	Group [☆]	Other*	Method [^]
aclonifen (H)	C	15	51:5
alachlor (H)	B	WF 10	51:5
aldrin (I)	A	0	51:5§
alpha-cypermethrin (I)	C	UP 23	51:5
atrazine (H)	B	WF, EP 11	51:5
DEA (M)			51:5
DIPA (M)			51:5
azoxystrobin (F)	C	UP 20	51:5
benazolin (H)	B	ÅT 5	50:8
bentazone (H)	C	UP 24	50:8
bitertanol (F)	C	21	51:5
carbosulfan (I)	C	15	51:5
carbofuran (I, M)	B	18	51:5
carfentrazone-ethyl (H)	C	UP 14	51:5
chlordan- γ (I)	A	0	51:5§
chlorfenvinphos (I)	C	WF, ÅT 9	51:5
chloridazon (H)	C	23	51:5
chlorpyrifos (I)	C	WF 20	51:5
cinidon-ethyl (H)	C	UP 11	51:5
clopyralid (H)	C	23	50:8
cyanazine (H)	C	ÅT 13	51:5
cyfluthrin (I)	C	UP 16	51:5
cypermethrin (I)	C	21	51:5
2,4-D (H)	B	UP 22	50:8
DDT-p,p (I)	A	0	51:5§
DDD-p,p (M)			51:5§
DDE-p,p (M)			51:5§
DDT-o,p (M)			51:5§
deltamethrin (I)	C	UP 24	51:5
dicamba (H)	C	23	50:8
dichlobenil (H)	B		51:5
BAM (M)			51:5
dichlorprop (H)	C	20	50:8
dicofol (I)	B		51:5
diflufenikan (H)	C	19	51:5
dimethoate (I)	C	23	51:5
diuron (H)	B	WF 15	51:5
α -endosulfan (I)	B	WF 14	51:5
β -endosulfan (I)		WF	51:5
endosulfan-sulfate (M)			51:5
esfenvalerate (I)	C	UP 19	51:5
ethofumesate (H)	C	UP 23	51:5
fenoxaprop-P (H)	C	21	50:8
fenpropimorph (F)	C	23	51:5
flamprop (H)	B	ÅT 9	50:8
fluroxypyr (H)	C	UP 21	50:8
flurtamone (H)	C	UP 9	51:5
heptachlor (I)	A	0	51:5§
heptachlor epoxide (M)			51:5
hexachlorobenzene (F, M)	A	WF 0	51:5§
hexazinon (H)	B	ÅT 8	51:5
imazalil (F)	C	UP 19	51:5
iprodione (F)	C	UP 22	51:5
isoproturon (H)	C	WF, UP 20	51:5
lambda-cyhalothrin (I)	C	UP 24	51:5
lindane (γ -HCH) (I)	A	WF, EP 0	51:5§
α -HCH (M)		WF	51:5§

Substance	Group [⊛]	Other*	Method [^]
β-HCH (M)		WF	51:5§
δ-HCH (M)		WF	51:5§
MCPA (H)	C	24	50:8
mecoprop (H)	C	UP 22	50:8
metalaxyl (F)	C	UP 24	51:5
metamitron (H)	C	23	51:5
metazachlor (H)	C	20	51:5
methabenzthiazuron (H)	C		51:5
metribuzin (H)	C	24	51:5
pendimethalin (H)	C	UP 23	51:5
permethrin (I)	C	EP	51:5
phenmedipham (H)	C	UP 24	51:5
pirimicarb (I)	C	20	51:5
prochloraz (F)	C	24	51:5
propiconazole (F)	C	UP 23	51:5
propyzamide (H)	C	UP 20	51:5
prosulfocarb (H)	C	11	51:5
pyraclostrobin (F)	C	UP 12	51:5
quinmerac (H)	C	14	50:8
simazine (H)	B	WF, EP 14	51:5
terbutryn (H)	B	ÅT 13	51:5
terbuthylazine (H)	B	21	51:5
DETA (M)			51:5
tolclofos-methyl (F)	C	16	51:5
tolyfluanid (F)	C	21	51:5
trifluralin (H)	B	WF 22	51:5
vinclozolin (F)	B	18	51:5

I = insecticide, H = herbicide, F = fungicide, M = metabolite. Metabolites are listed with their respective mother substance.

⊛ Substances are divided into the following categories (with the exception of metabolites, 13):

A = Prohibited within the EU (6).

B = Not registered for use in Sweden, but registered in other EU countries (17).

C = Registered for use in Sweden (49).

* Abbreviations as below. Figures state the number of countries within EU the pesticide was registered for use in November 2004.

WF = Priority substance of the Water Framework Directive, Appendix X.

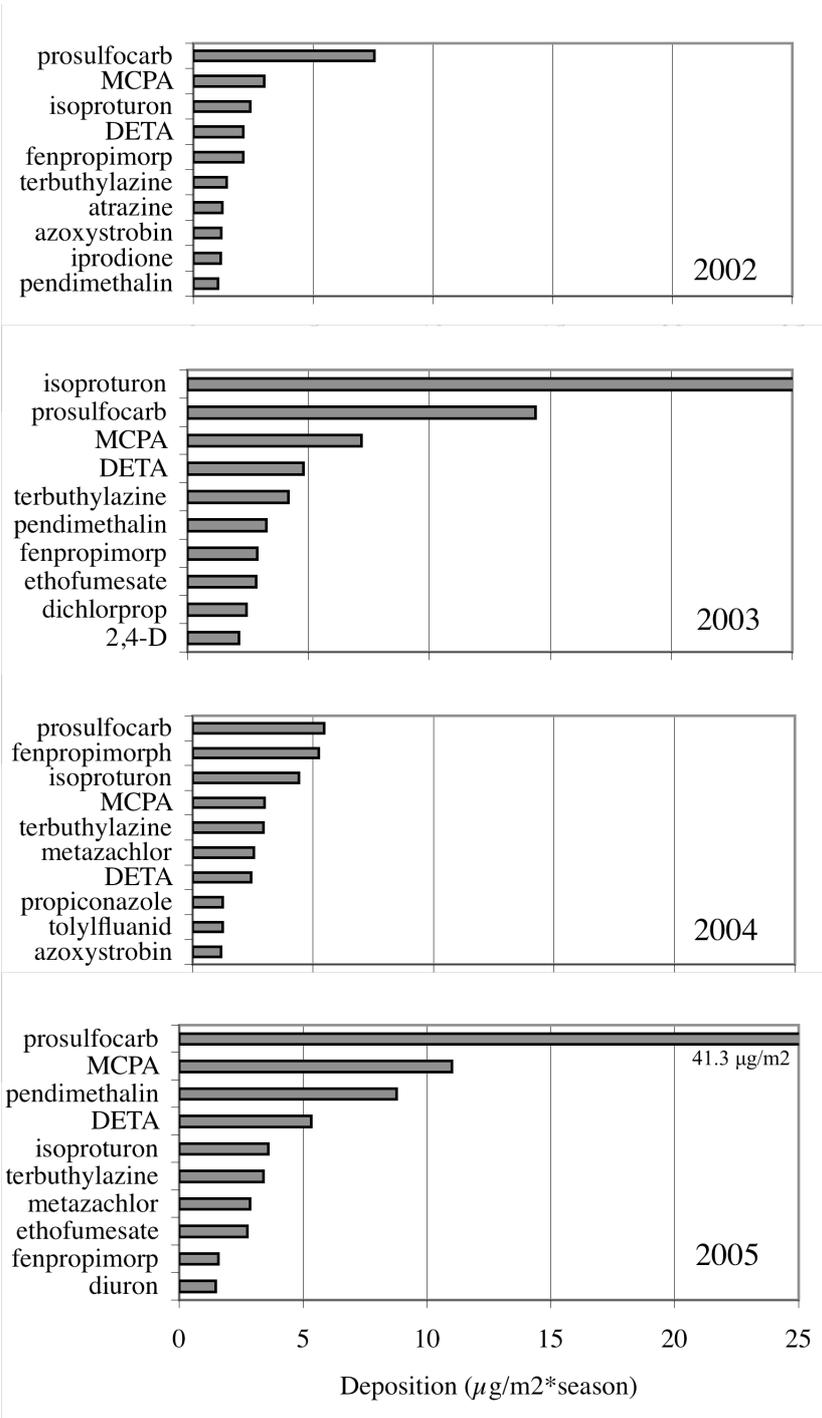
UP = On the Annex 1 list, i.e. a general registration within the EU.

EP = Banned within the EU, was not accepted for inclusion on the Annex 1 list (some countries have an exemption).

ÅT = Banned within the EU since July 2003, no application for an Annex 1 registration (some countries have an exemption).

[^] Analytical method OMK 51:5 (semi- and non-polar substances) and analytical method OMK 50:8 (polar substances)

§ extra clean-up procedure



Appendix 3. Pesticides with the highest seasonal (four months) deposition each year.

Appendix 4. Summary of the most volatile pesticides included in the monitoring study

Vapour pressure (Pa)	Pesticide
0.1 - 1	dichlobenil
0.01 – 0.1	tolclofos-methyl
0.001 – 0.01	alachlor, chlordane, chlorpyrifos, clopyralid, dicamba, fenpropimorph, hexachlorobenzene, lindane, pendimethalin, prosulfocarb, trifluralin

Source: Pesticide Manual (Tomlin, Ed.)