

Results from the Swedish National Screening Programme 2004

Subreport 5: Mirex and Endosulfan

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<p>Title and subtitle of the report Results from the Swedish National Screening Programme 2004 Subreport 5: Mirex and Endosulfan</p>	
<p>Summary Measurements of the pesticides mirex and endosulfan were performed in 49 samples of air, deposition, sediment, sludge, water and biota at background sites and at diffuse sources. Mirex was not detected in any of the samples analysed, and was concluded not to occur in elevated concentrations in the Swedish environment. Endosulfan and endosulfan sulphate were detected in air and deposition and the latter also in sediments, biota and leachate water. Endosulfan seems to mainly enter the environment via long-range atmospheric transport. There may be other diffuse emissions resulting in observed levels of endosulfan sulphate. In order to address remaining questions, further analysis of e.g. outgoing sewage water, sewage sludge, biota and/or food stuffs as well as regular air monitoring of endosulfan is suggested.</p>	
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Sammanfattning

IVL har på uppdrag av Naturvårdsverket utfört en ”screeningstudie” av pesticiderna mirex och endosulfan. Båda dessa ämnen är förbjudna i Sverige, och användningen av mirex var begränsad även innan förbudet. Både mirex och endosulfan är dock kända för att ha potential för långväga atmosfärisk transport, vara potentiella ”PBT-ämnen” (Persistenta, Bioackumulerande, Toxiska) och ingår på olika internationella prioriteringslistor. Det är därför av intresse att kartlägga förekomsten av dessa två ämnen i den svenska miljön.

Huvudsyftet med studien var att bestämma koncentrationer i olika matriser i miljön, att belysa viktiga transportvägar samt att bedöma sannolikheten för pågående emissioner i Sverige. Ett ytterligare syfte var att bedöma omfattningen av atmosfärisk transport samt upptag i biota. Studiens resultat skall kunna bidra med underlag för beslut om vidare miljöövervakning av dessa ämnen.

En provtagningsstrategi utarbetades utifrån ämnenas fördelningsegenskaper samt möjliga källor till utsläpp. Inga primära punktkällor kunde identifieras inom landet, varför endast bakgrundsstationer, diffusa källor (reningsverk) samt urbana stationer valdes ut. För endosulfan analyserades dessutom tre prover av lakvatten från kompost samt deponi. Två länsstyrelser deltog i studien och bidrog med ytterligare prover för analys. Tabellen nedan visar det totala antalet prover som analyserats inom studien, där M = mirex och E = endosulfan.

Program	Luft		Deposition		Vatten		Sediment		Slam		Biota		Totalt	
	M	E	M	E	M	E	M	E	M	E	M	E	M	E
Nationellt	11	11	11	11	-	3	11	11	3	3	6	6	42	45
Regionalt						1	2	2	1	1			3	4
Totalt	11	11	11	11	-	4	13	13	4	4	6	6	45	49

Mirex kunde inte detekteras i något av de prover som analyserats. Detektionsgränserna låg i samma nivå som uppmätta koncentrationer av andra miljöföroreningar i området. Dessa mätningar indikerar att mirex inte förekommer i förhöjda halter i den svenska miljön i jämförelse med andra välkända miljöföroreningar.

Såväl α - som β -endosulfan samt omvandlingsprodukten endosulfan-sulfat återfanns i luft och deposition i ungefär samma nivåer som pesticiden hexaklorcyklohexan (HCH), och uppvisade samma säsongsvariation både på västkusten och i norra Finland. Koncentrationerna av endosulfan i urban luft var i samma storleksordning som vid bakgrundsstationerna, vilket tyder på begränsad betydelse av diffusa lokala utsläpp till luft. Endosulfan kunde ej detekteras i biota eller sediment, men den mer stabila omvandlingsprodukten endosulfan-sulfat hittades i sediment, såväl som i ett biotaprov samt i lakvatten från kompost.

Endosulfan uppvisar ett mönster som indikerar att den huvudsakligen transporteras till den svenska miljön på ett sätt som liknar det för hexaklorcyklohexaner, dvs via långväga atmosfärisk transport följt av deposition.

Med tanke på den observerade förekomsten i atmosfären, att koncentrationerna är i nivå med koncentrationer av andra POPs (persistent organic pollutants) samt indikationerna om långväga transport som huvudsaklig emissionsväg i Sverige, skulle regelbunden övervakning av endosulfan i luft vara värdefull för att bevaka trenderna i den svenska atmosfären.

Förekomsten av endosulfan-sulfat i lakvatten från kompost samt i urbana sediment och det faktum att de sistnämnda uppvisade högre koncentrationer än motsvarande bakgrundsprover, skulle kunna vara en indikation om möjliga andra diffusa emissioner via t ex reningsverk eller dagvattensystem. Vidare analys av t ex utgående avloppsvatten, slam och eventuellt även olika potentiellt kontaminerade livsmedel skulle kunna belysa denna fråga. Dessutom skulle ytterligare analys av biota kunna ge information om den generella förekomsten av endosulfan och/eller dess omvandlingsprodukter i svensk biota.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a screening study of the pesticides mirex and endosulfan. These chemicals are both banned in Sweden, and the use of mirex has been limited also in the past. However, both of these substances are known to undergo long-range transport, they are potential P/B/T (Persistent, Bioaccumulative, Toxic) substances and they are included on international priority lists. Thus, it is of interest to map the present occurrence of these substances in the Swedish Environment.

The overall objectives of the screening were to determine concentrations in a variety of environmental media in Sweden, to highlight important transport pathways and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport and uptake in biota. The outcome of the study is aimed to serve as a basis for decision-making regarding monitoring activities of these chemicals.

A sampling strategy was set up based on the partitioning properties and possible sources of these compounds. No primary point sources could be identified within the country for any of the two chemicals, thus only background sites, diffuse sources (sewage treatment plants) and urban sites were selected. For endosulfan, three additional samples of compost and landfill leachate were analysed. Two county administrative boards participated in the study and provided additional samples for analysis. The total number of samples analysed in the study are shown in the table below, where M = mirex and E = endosulfan.

Programme	Air		Deposition		Water		Sediment		Sludge		Biota		Total	
	M	E	M	E	M	E	M	E	M	E	M	E	M	E
National	11	11	11	11	-	3	11	11	3	3	6	6	42	45
Regional						1	2	2	1	1			3	4
Total	11	11	11	11	-	4	13	13	4	4	6	6	45	49

Mirex was not detected in any of the samples analysed. The detection limits were in the same range as measured concentrations of other pollutants in the area. These measurements indicate that mirex does not occur in elevated concentrations in the Swedish environment in comparison to other pollutants.

Both α - and β -endosulfan and the transformation product endosulfan sulphate were detected in air and deposition in the same range as the pesticides hexachlorocyclohexanes (HCHs), and with the same seasonal variation, both at the Swedish west coast and in the north of Finland. The concentrations of endosulfan in urban air were similar to those at the background stations, implying low impact of diffuse local emissions to air. Endosulfan was not detected in biota or sediments, but the stable transformation product endosulfan sulphate was found in sediments, as well as in one biota sample and in compost leachate water.

On the whole, endosulfan shows a pattern indicating that it mainly enters the Swedish environment in a similar manner as HCHs, i.e. via long-range atmospheric transport followed by deposition.

Considering the common occurrence in the Swedish atmosphere, the fact that levels are similar to those of other POPs (persistent organic pollutants) and the indications of long-range transport as the major emission source of endosulfan in Sweden, it is suggested that endosulfan is regularly monitored in air for at least a few years time, in order to give information about the temporal trends of endosulfan in Swedish air.

Endosulfan sulphate occurred in compost leachate and in urban sediments, the latter showing higher concentrations than corresponding background samples. This may be a sign of possible diffuse emissions through sewage systems or storm water, which may arise from e.g. consumption of contaminated food followed by transformation to endosulfan sulphate. Further analysis of e.g. outgoing sewage water, sewage sludge, and/or foodstuffs would help addressing this issue. Additionally, further measurements of biota samples would provide information about the general occurrence in Swedish biota.

Table of contents

Sammanfattning.....	1
Summary	3
1 Introduction.....	7
2 Chemical properties, toxicity and fate.....	9
2.1 Mirex.....	9
2.2 Endosulfan.....	10
3 Production, use, emissions and regulation	13
3.1 Mirex.....	13
3.2 Endosulfan.....	13
4 Previous measurements in the environment.....	15
4.1 Mirex.....	15
4.2 Endosulfan.....	16
5 Sampling strategy and study sites.....	17
5.1 National.....	17
5.2 Regional.....	19
6 Methods	20
6.1 Sampling.....	20
6.1.1 Air and deposition.....	20
6.1.2 Water	21
6.1.3 Sediment.....	21
6.1.4 Sludge	21
6.1.5 Fish	21
6.2 Analysis.....	22
6.2.1 Chemicals.....	22
6.2.2 Extraction	22
6.2.3 Clean-up of sample extract	22
6.2.4 GC-MS analysis.....	23
7 Results and discussion	24
7.1 National.....	24
7.1.1 Mirex.....	24
7.1.2 Endosulfan	24
7.2 Regional.....	29
8 Conclusions	30
9 Acknowledgements	30

10	References.....	32
	Appendix. Information on samples and lists of results	

1 Introduction

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a "Screening Study". This screening, which was carried out during 2004/2005, includes the following substances: adipates, octachlorostyrene, limonene, siloxanes, mirex, endosulfan and isocyanates. The different substances or groups of substances are emitted to and spread in the environment via a variety of sources, e.g. point sources and use in products. Some of the chemicals are commonly used internationally and/or in Sweden.

The seven chemicals or chemical groups studied have been identified as potentially toxic, bioaccumulative and/or persistent. Some are also included on different international/national priority lists. Table 1 shows an overview of the chemicals included and the major reasons for their concern.

Table 1. Overview of chemicals included in the screening 2004 and the reason for their concern (Loh et al., 2003; Andersson, 2004; OSPAR, 2005; UNEP, 2005). The chemicals considered in the current report are written in bold/italic letters.

Chemical	Chemical type	Banned/ Restricted	HPV ^a	Indications of toxicity	Evidence for B/P ^b	International Priority List
Adipates	Additive	No	X	X		
Octachlorostyrene	Unintentional by-product	PRIO- substance ^c		X	X	Candidate for the Stockholm convention
Limonene	Cleaning agent (also naturally occurring) Lubricant, industrial raw material,			X		
Siloxanes	chemical additive	PRIO- substance ^c	X	X	X	OSPAR (HMDS)
Mirex	Pesticide	Banned		X	X	Stockholm convention WFD, OSPAR, Candidate for the Stockholm convention
Endosulfan	Pesticide	Banned		X	X	
Isocyanates	Industrial raw material	Regulated	X	X		OSPAR ^d

^a) High Production Volume

^b) Bioaccumulation/Persistence

^c) The chemical is included on Swedish Chemicals Inspectorate's PRIO-list, and is identified as a "phase-out-chemical"

^d) Concerns 3,3'-(ureylenedimethylene)-bis-(3,5,5-trimethylcyclohexyl) diisocyanate

The overall objectives of the screening were to determine concentrations in a variety of environmental media in Sweden, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport and uptake in biota. The outcome of the study is aimed to serve as a basis for decision-making regarding monitoring activities of these chemicals.

Due to the variety in emission sources and use as well as differences in chemical properties, the screening has been carried out in seven sub-projects. This report considers the results of **mirex and endosulfan**. Results for the other chemicals are presented in subreports 1-4 and 6.

2 Chemical properties, toxicity and fate

2.1 Mirex

Mirex, or dechlorane, is a white crystalline, odourless solid with physical-chemical properties according to Table 2. Its chemical structure is shown in Figure 1. Mirex is considered to be very persistent in the environment, with a half-life of up to 10 years (UNEP, 2005). It is non-reactive with both acids and bases and is fairly resistant to pyrolysis (decomposition beginning at 525°C), where formation of hexachlorobenzene may take place. Slow partial decomposition may result from exposure to ultraviolet radiation or to gamma rays, resulting in the formation of mainly photomirex (8-monohydro-mirex) (WHO, 1984). Biodegradation of mirex does generally not occur, but it may take place under anaerobic conditions in e.g. sewage sludge (WHO, 1984).

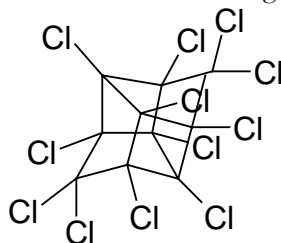


Figure 1. Chemical structure of mirex (CAS no 2385-85-5)

Mirex is a semivolatile substance, which means that in the atmosphere, it can exist in both the vapour and particulate phases. It has properties classifying it as a “POP” (persistent organic pollutant), implying a large potential for atmospheric long-range transport.

The major removal mechanism for POPs from the air is via wet and dry deposition, which may take place far away from the original sources. Atmospheric deposition is an important pathway for mirex to both aquatic and terrestrial ecosystems. As a result of the atmospheric deposition, mirex may accumulate in the upper soil layer where it is regarded as practically immobile; thus transport from soil is unlikely. In water, mirex will mainly be associated with particles, and is thus likely to quickly deposit to and accumulate in sediments (WHO, 1984).

A modelling exercise was performed using the Equilibrium Criterion (EQC) model (Mackay et al., 1996) in order to highlight likely fate and partitioning behaviour of mirex. Physical-chemical properties were taken from Table 2, as given in SRC (2005) and degradation half-lives were taken from Mackay (2001), air 170 h, water 170 h, soil 55000 h and sediment 55000 hours. Emission rates were set to 1000 kg/h, only for illustrative purposes. The outcome of the modelling exercise is shown in Table 3, together with the results for endosulfan.

The results are indicative, as the partitioning behaviour is dependent on model structure as well as chemical property data and may be different in a different environment. It is, however, evident that the “persistence” (system residence time) of mirex is very high, and system removal is expected to occur mainly via advective processes (i.e. transport out in air and water) rather than via degradation. Regardless of emission media, mirex is predicted to partition to soil and sediments, and only trace amounts will be found in other media. When emitted only to air, a larger proportion is predicted to

partition to air, and may thus be available for advection out of the system. On the whole, this exercise emphasises the long residence time of mirex and its low mobility when released to soil. It should be noted that the historical use of mirex has primarily been as a pesticide within agriculture, which implies that soil has been the primary receiving media in the past.

Mirex is classified as “possibly carcinogenic to humans”. It has endocrine disruptive properties and is very toxic to aquatic organisms and to rodents, with acute neurological effects on the latter such as muscle tremors, diarrhea, depression and death (WHO, 1984). US EPA has adopted an oral reference dose of 0.2 µg/kg/day. Short-term studies resulted in observed effects such as weight loss, induction of mixed function oxidases, morphological changes in liver cells and sometimes death (WHO, 1984). Mirex is known to bioconcentrate and to biomagnify. Therefore, the substance poses a potential risk to organisms on higher trophical levels. Because of its high persistence, environmental levels can be expected to remain high for a long time, even though consumption has ceased.

Table 2. Physical-chemical properties of mirex and endosulfan

Substance	MW (g/mol)	MP (°C)	W _{SOL} (mg/L)	V _F (Pa)	H (Pa m ³ /mol)	logK _{OW}	logK _{OC}	BCF ^a
Mirex	545	485 ^a	Insoluble ^a 0.085 ^b 0.00065 ^c	4 × 10 ⁻⁵ , ^a 1.06 × 10 ⁻⁴ , ^b 1.0 × 10 ⁻⁴ , ^c	52.28 ^a 82.17 ^b	5.28 ^a 6.9 ^b	7.4	Algae: 12200 Fish: 2580
Endosulfan	407	106 ^a	α- 0.53; β- 0.28 (25°C) ^a 0.32 ^b	8.25×10 ⁻⁴ , ^a 2.3×10 ⁻⁵ , ^b	6.69 ^a 6.59 ^b	3.83 ^{a,b}	3.3 (soil) ^a 3.6 (sed) ^a	2650 11583
Endosulfan sulphate	423	181- 182 ^a	0.117 mg/L ^a 0.48 mg/L ^b	1.33×10 ⁻⁹ , ^a 3.5×10 ⁻⁵ , ^b		3.66 ^a		

^aHSDB 2005 ^bSRC, 2005 ^cMackay, 2001.

2.2 Endosulfan

Endosulfan occurs in the form of brown crystals, and has a slight sulfur dioxide odour. Technical grade endosulfan contains two isomers, α- and β-endosulfan, in the ratio 7:3 respectively (make up 94 % of the content). α-Endosulfan is composed of an enantiomeric pair (Schmidt et al., 1997). The impurities in the technical product are reported to be endosulfan alcohol (2 %) and endosulfan ether (1%) (Maier-Bode, H., 1968 in Schmidt et al. 2001). β-Endosulfan has been reported to slowly rearrange to the more stable form α-endosulfan in the environment (Schmidt et al. 2001). Endosulfan sulphate is an oxidation product found in technical endosulfan but is also a microbial oxidation product of α- and β-endosulfan (Walse et al. 2002). Properties are listed in Table 2, and chemical structures are shown in Figure 2.

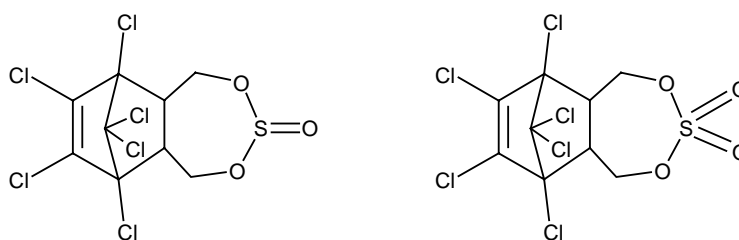


Figure 2. Chemical structures of endosulfan (CAS no 115-29-7) and endosulfan sulphate (CAS no 1031-07-8)

Walse et al. (2002) identified endosulfan diol as the main degradation product of α - and β -endosulfan in the aqueous environment, in the presence of various catalytic metal oxides. No endosulfan sulphate was detected under these conditions. Other metabolites, which were in minor amounts, were endosulfan ether, endosulfan lactone and endosulfan hydroxyether. Endosulfan sulphate was observed to be stable in the presence of mentioned metal oxides. Endosulfan sulphate has shown to be the main microbial oxidation product of endosulfan (Sutherland et al. 2000 in Siddique et al., 2003). Siddique et al. (2003) reported that some fungal and bacterial strains have the ability to degrade α - and β -endosulfan to endosulfan diol and endosulfan ether, while these strains did not produce endosulfan sulphate. Gonzalez et al. (2003) observed oxidation of endosulfan in soil samples resulting in endosulfan sulphate concentrations that were 400 times higher than the mother compounds α - and β -endosulfan. This was also observed in standing crops cultivated on the soil.

Like mirex, endosulfan is a semivolatile substance, classified as a POP, and as such may exist in both the vapour and particulate phases of the atmosphere and has potential for long-range transport. According to van Drooge et al. (2004), endosulfan is predominantly found in the gas phase, where it may react with hydroxyl radicals, with an estimated half-life of 2 days (HSDB, 2005). Photolysis is also possible, although the reaction kinetics are unknown.

Similar to mirex, atmospheric deposition is an important pathway for endosulfan. When deposited to soil, endosulfan is regarded to be fairly immobile (K_{OC} of 2,000), but volatilisation from moist soil surfaces may occur. Biodegradation may take place, with reported half-lives of 32 and 150 days in aerobic and anaerobic soils, respectively (HSDB, 2005). Endosulfan is less stable in the environment than mirex, albeit it is still considered to be persistent (e.g. OSPAR, 2005).

In aquatic systems, the K_{OC} -value ($\log K_{OC}$ in sediments of 3.6; see Table 2) indicates that endosulfan may adsorb to suspended solids and deposit to sediments. However, the relatively high water solubility also implies that a certain proportion is likely to remain in the water column. Volatilisation from water surfaces is possible, based on the Henry's Law constant. Biodegradation may also take place in water, with reported half-lives of 2 and 8 days in aerobic and anaerobic waters respectively. Endosulfan may also undergo hydrolysis (half-lives of 9 to 533 h) (HSDB, 2005).

A modelling exercise similar to that for mirex (see chapter 2.1) was performed also for endosulfan. Physical-chemical properties were taken from Table 2, as given in SRC (2005). The degradation half-lives used were as follows: air 5 h, water 55 h, soil 1700 h and sediment 550 h, all based on degradation data obtained from various sources (e.g. ECE, 2003; HSDB 2005) and classified according to Mackay (2001). Emission rates were set to 1000 kg/h. The outcome of the modelling exercise is shown in Table 3.

Table 3. Results from EQC modelling of mirex (M) and endosulfan (E), using emission rates of 1000 kg/h

Emission medium	Percentage in air		Percentage in water		Percentage in soil		Percentage in sediment		Persistence (h)	
	M	E	M	E	M	E	M	E	M	E
Air	38	32	<0.1	1	56	67	5	<0.1	184	21
Water	<0.1	<0.1	1.5	98	<0.1	<0.5	98.5	1.5	9500	74
Soil	<0.0	<0.0	<0.0	<0.1	99.9	100	<0.1	<0.0	76 000	2400
All three	<0.5	<0.5	<0.5	3	89	97	11	<0.1	29 000	840

The modelling results confirm that the persistence of endosulfan is much lower than that of mirex (Table 3), which is expected, considering the lower degradation half-lives. Relative to mirex, the partitioning behaviour of endosulfan is more dependent on mode of release, i.e. emission to water will result in partitioning to water etc. In this case, a small amount is predicted to partition to sediments. The exercise emphasises that the partitioning behaviour of endosulfan is dependent on the release pattern and it shows that the residence time in the environment is relatively short compared to chemicals such as e.g. mirex. It should be noted that like mirex, the historical use of endosulfan has primarily been as a pesticide within agriculture, which implies that air and soil have been the primary receiving media in the past, and still are in some countries.

Endosulfan has not been classified as carcinogenic to humans, but has been shown to induce acute effects such as headache, dizziness, nausea, tremors and unconsciousness. It is toxic to rodents, with reported LD₅₀ values of 18 mg/kg (oral) for rats and 7.4 mg/kg (oral) for mice. Endosulfan has a high tendency to bioconcentrate in aquatic organisms, with reported bioconcentration factors (BCF) of 2650 and 11583. Thus, the substance poses a potential risk to organisms on higher trophical levels (HSDB, 2005).

3 Production, use, emissions and regulation

3.1 Mirex

Mirex has previously been widely used as an insecticide, as fire ant repellent in the U.S., but also as a flame retardant (in e.g. plastics, rubber, paints etc.). It was first synthesised in 1946 but was not used as an insecticide until 1955. Technical grade of mirex contains 95 % mirex and 2.6 % chlordecone, while the rest is unspecified (WHO, 1984). Its toxic effects were widely realised in the seventies, and it was banned in several nations; e.g. U.S. 1977, Canada 1978, Mexico 1982, New Zealand 1988, and Argentina 1999. In the year of 2000, mirex was still used in Australia (Rappe, 2000).

Mirex is included in the set of chemicals known as "The Dirty Dozen", for which the use and dispersion should cease according to the decision by UNEP at the environmental conference in Rio de Janeiro 1992. An agreement aimed to ban these 12 chemicals was signed by 151 countries at the Stockholm convention 2001 (UNEP, 2005). Sweden ratified this protocol in 2002. There is no registered use in Sweden.

On a global scale, primary emission of mirex to air is likely to occur both at production sites and during the application as an insecticide. However, these emission pathways should be limited today, as the global use of mirex is restricted. Emission to air may also occur through combustion of mirex-containing goods and through evaporation from landfills containing such products. As the application of mirex is in the form of spray, the immediate and direct uptake in soil should be limited (WHO, 1984). Direct emission to water is unlikely to occur but it may be transported to water bodies from agricultural areas and via sewage water from production sites. The major transport pathway to water bodies is most likely via atmospheric deposition.

In Sweden, there are no primary emissions of mirex, thus the main transport pathway to the Swedish environment is likely to be atmospheric long-range transport followed by deposition to soil and water bodies.

3.2 Endosulfan

Endosulfan is a broad spectrum insecticide used to treat vegetables, tea, berries, trees, woody plants, cereals, tobacco, rice, sweetcorn, grapes, fruit, potatoes, cotton etc. (Schmidt, 2001; US EPA, 2005). Endosulfan is formulated as a liquid emulsifying concentrate and wetting powder. It is applied by dip treatment, ground or air spraying from aircraft. The annual use in the U.S. is estimated to 640 000 ton of active substance (U.S. EPA, 2005). Crops that are treated to a great extent are squash, cantaloupe and pumpkins. In terms of applied amounts the most important crops are pecans, honeydews and strawberries (U.S. EPA 2005). In Sweden, the last approved use ceased in 1995. Previously, use has occurred in three forms, under the trade name "cyclodan" (www.kemi.se). According to UNECE (2004), use of endosulfan still occurred as late as 1999 in several European countries such as Belgium, France, Switzerland, Spain, Italy and Greece. The total European use of endosulfan in 1999 was estimated to 470 metric tonnes (UNECE, 2004). No later statistics have been obtained.

The historical global production and use of endosulfan as an insecticide has resulted in its direct release to the environment. In Sweden today, endosulfan is likely to enter the environment mainly via atmospheric long-range transport, followed by deposition to soil and water bodies (see chapter 5). Another source for endosulfan in Sweden may be through import of contaminated food (e.g. Loh et al., 2003).

4 Previous measurements in the environment

4.1 Mirex

Most previous studies deal with the occurrence of mirex in aquatic species and in foodstuffs, which is logical considering its high potential for bioaccumulation, and thus likelihood of being found in biotic tissues. Data also exist on mirex in sediments. No studies have been found in the literature concerning the occurrence of mirex in air, although the atmosphere has been pointed out to be one of the major media of long-range transport. Only few studies concerning the occurrence of mirex in surface water are available. One study reports the occurrence of mirex in Baltic species – see Table 4.

Table 4. Measured concentrations of mirex in various matrices in the environment. ww=wet weight, lw= lipid weight, nd = not detected

Type of sample	Site	Concentration	Reference
Water ($\mu\text{g/L}$)			
Water	USA, after application, 1973	0.0001	WHO, 1984
Pond water	USA, after application, 1974	0.2 and 0.53	WHO, 1984
Rural drinking water	USA, 1978	nd – 0.44	WHO, 1984
Sediment ($\mu\text{g/kg}$)			
Lake sediment	USA, Lake Ontario, early 80's	nd-62	HSDB, 2005
River sediment	USA, Niagara River, early 80's	12 (average)	HSDB, 2005
River sediment	USA, Rockaway River, mid 80's	0.1-80	HSDB, 2005
Dregged sediment	USA, Bayley Creek, mid 70's	133000	HSDB, 2005
Biota (mg/kg)			
Baltic herring	Bothnian Bay	0.00048 (lw)	Strandberg et al.1998
Baltic herring	Bothnian Sea	0.0014 (lw)	Strandberg et al.1998
Perch	Bothnian Bay	0.0008 (lw)	Strandberg et al.1998
Perch	Bothnian Sea	0.0014 (lw)	Strandberg et al.1998
Ale wife	Lake Ontario 1976 – 2000	0.19-0.01 (ww)	Makarewicz et al., 2003
Yellow perch	Lake Ontario 1976 – 2000	0.08-0.001 (ww)	Makarewicz et al., 2003
Zooplankton	Lake Ontario 1976 – 2000	0.0035 – 0.0002 (ww)	Makarewicz et al., 2003
Fish	Lake Ontario	Up to 0.27 (ww)	WHO, 1984
Foodstuffs (mg/kg)			
Beef	USA (area where mirex has been used)	mean: 0.026 (lw)	WHO, 1984
Fish and other aquatic organisms	USA (area with high levels in sediment)	nd – 0.97 (ww)	WHO, 1984
Others (mg/kg)			
Human milk	Canada	0.002- 0.02215 (lw)	WHO, 1984

4.2 Endosulfan

Several studies have been performed concerning the occurrence of endosulfan and transformation products in air and deposition (see Table 5). In recent investigations endosulfan/endosulfan sulphate has been detected in both air and deposition also at background areas.

In Sweden, measurements of endosulfan have been carried out recently by Ulén and Kreuger (2000). However, detectable levels of α - and β -endosulfan were only found in one of approximately 1500 water samples, and endosulfan sulphate in four out of 1500 samples (reference cited in Loh et al., 2003).

Reported measurements of endosulfan in biota are rare. Falandysz et al. (2001) analysed the soft tissue of blue mussel, crab and fish collected from different sites in the Gulf of Gdańsk. Many of the classical pesticides were detected. Endosulfan was analyzed for but not found.

Table 5. Measured concentrations of endosulfan and endosulfan sulphate in various matrices in the environment.

Type of sample	Site	Concentration	Reference
Air ($\mu\text{g}/\text{m}^3$)			
	Central Pyrenees	1.0 – 6.6 (α -), 0.5 –1.6 (β -)	van Drooge et al., 2004
	High Tatras	1.4 – 42.8 (α -), 0.7 –7.5 (β -)	van Drooge et al., 2004
	Langley, Aug 2001	3.5 – 154 (α -), 12 – 107 (β -)	Harner et al., 2005
	Slocan, Aug 2001	3.0 – 39 (α -), 2.3 –51.5 (β -)	Harner et al., 2005
Deposition ($\text{ng}/\text{m}^2 \text{ month}$)			
	Estany Redó, Pyrenees	340 (α -, β - , -sulphate)	Carrera et al., 2002
	Gossenköllsee, the Alps	190 (α -, β - , -sulphate)	Carrera et al., 2002
	Øvre Neadalsvatn, Caledonian mountains	0.2 (α -, β - , -sulphate)	Carrera et al., 2002
Biota ($\text{ng}/\text{g lipids}$)			
Various aquatic species	Gulf of Gdańsk	<3 (α - and β -)	Falandysz et al., 2001

5 Sampling strategy and study sites

5.1 National

A national sampling strategy was developed in order to determine the environmental concentrations of mirex and endosulfan in different environmental matrices in Sweden. An additional aim of the sampling was to identify major emission sources as well as important transport pathways. A screening programme normally includes both measurements in background areas and close to identified potential point sources. Measurements of diffuse emission pathways from the society such as sewage systems and urban areas are normally also included. The sampling programme for mirex and endosulfan was focused on measurements at background sites.

In order to determine environmental background levels, air, deposition, sediment and biota samples were collected. The locations of the sampling sites are shown in Figure 3. The sampling stations Råö (Swedish west coast) and Pallas (in northern Finland) are also a part of the national monitoring program for air pollutants and included in the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) and Arctic Monitoring and Assessment Programme (AMAP) networks. The sediment samples were collected at off shore stations in the Baltic Sea (SGU Ingemar Cato – see chapter 6.1.3). The biota samples were collected at background sites used within the national monitoring programme for contaminants in biota (NRM Anders Bignert –see chapter 6.1.5).

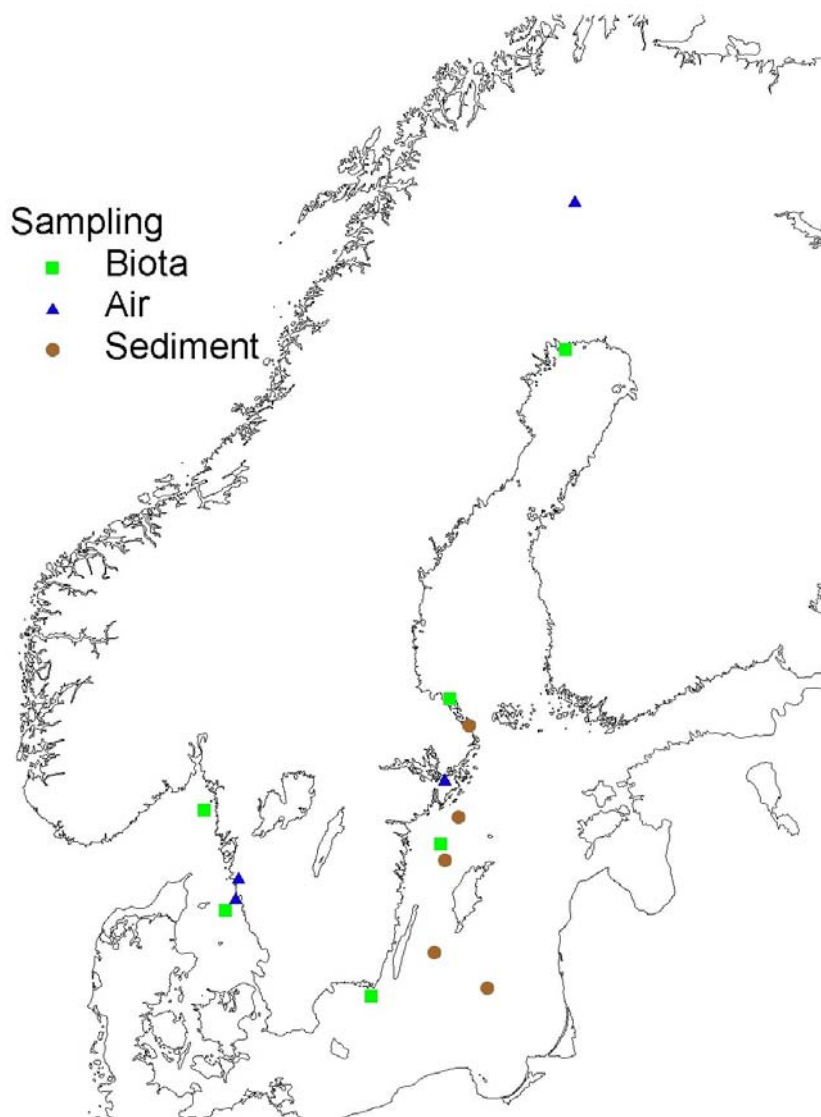


Figure 3. Geographic distribution of background and urban sampling stations. Not all stations were used in all subprojects – see Appendix for detailed information about samples.

In the case of mirex, no obvious point sources could be identified within Sweden. As diffuse sources three sewage treatment plants (STPs) and one urban site in central Stockholm were selected. The STPs are all included in the Swedish Environmental Protection Agency's monitoring programme for environmental pollutants in sludge (Naturvårdsverkets miljöövervakningsprogram av miljögifter i slam) (Table 6). For endosulfan, three additional samples of leachate were taken, one from a landfill in Upplands Bro, and two from compost leachate in Borlänge and Västerås.

Table 6. National sampling strategy for mirex (M) and endosulfan (E)

	Air		Deposition		Water		Sediment		Fish		Sludge		Total	
	M	E	M	E	M	E	M	E	M	E	M	E	M	E
Background														
Råö	4	4	4	4									8	8
Pallas	4	4	4	4									8	8
Various							5	5	6	6			11	11
Diffuse sources														
STP Henriksdal											1	1	1	1
STP Eslöv											1	1	1	1
STP Floda											1	1	1	1
Landfill leachate (Högbytorp)					1								-	1
Compost leachate (Borlänge, Västerås)					2								-	2
Urban (Stockholm)	3	3	3	3			6	6					12	12
Total	11	11	11	11	3		11	11	6	6	3	3	42	45

5.2 Regional

Regional screening was carried out by different Swedish county administrative boards that had the possibility to collect samples to send to IVL for analysis. Different counties have chosen different strategies for their own regional sampling scheme. The selection of the "regional" samples was meant to increase the number of samples for substances connected to their environmental programmes i.e. substances that have been regulated or included in the national priority database. Another strategy has been to choose substances where environmental levels are expected to differ from national levels because of intense use within the county i.e. local industrial areas or because of geographic proximity to European industrial areas.

Two different county administrative boards participated in the regional sampling programme of mirex and endosulfan with a total of four extra samples: two sediment samples, one sludge sample and one water sample.

6 Methods

6.1 Sampling

As a guideline for adequate and consequent sampling, a manual for the sampling personnel in the national as well as the regional screening programmes was developed. Detailed instructions for sampling, storing and transport were given. Sampling protocols for all sample types were included in the manual. The overall aim of the sampling protocols was to:

1. Guide the responsible personnel on how to avoid contamination when sampling
2. Ensure documentation of the sampling procedure, quality of the sample and environmental and physical circumstances during the sampling.

The samples from the regional county administrative boards were sent to IVL Swedish Environmental Research Institute for analysis. Details of all samples are given in Tables A1-A3 in Appendix 1.

6.1.1 Air and deposition

Urban air samples were collected using a low volume air sampler (LVS) with a flow of approximately 1 m³/hour. Particles were collected on a glass fibre filter (MG160, Munktell) and substances in the gas phase with the adsorbents XAD-2 (Amberlite) and polyurethane foam (PUF), which were packed in two glass columns in series. The sampling duration was two weeks. Filter and adsorbents were changed after one week. Air samples at the background stations were collected using a high volume air sampler (HVS) with a flow of approximately 25 m³/hour. Substances in the particle phase were collected on a glass fibre filter (MG160, Munktell) and in the gas phase on an adsorbent (PUF-plugs). The sampling was carried out for one week and four weekly samples were pooled to represent an average for one month. Prior to sampling the filters were heated to 350°C, and the adsorbent columns were cleaned by Soxhlet extraction with acetone. After sampling the filters and columns were wrapped in aluminium foil and sent to the laboratory where it was stored in a freezer (-18°C) until analysis. An additional filter and column used as a field blank was sent back to the laboratory unexposed.

The quality of the air sampling procedure was checked. Deuterated endosulfan was injected onto the first adsorbent column of two in series and an urban air sample (~ 170 m³) was collected according to the protocol. Analysis was performed as described below. This control revealed that (a) endosulfan was stable on the column and was not sensitive to oxidation agents in the air (e.g. ozone), (b) no breakthrough was detected and (c) the recovery was quantitative.

Both wet and dry deposition was collected using an open sampler (bulk sampler). This sampler consists of a 1 m² Teflon coated surface with 10 cm high edges. The bottom declines slightly to a central opening where a cassette with an adsorbent (PUF) is attached. The deposition sample includes both compounds in the precipitation and compounds deposited to the collection surface of the sampler. Both the precipitation and the deposited particles are included in the analysis. This

type of sampler is used for deposition measurements of organic contaminants within the Swedish national monitoring of air pollutants (Brorström-Lundén, 1996).

6.1.2 Water

Water samples were collected in pre-heated (400°C) glass bottles fitted with aluminum foil lined screw caps and stored in a refrigerator until analysed. A bottle with ultra pure water (Milli-Q), which was exposed to the surrounding environment during the sampling time, was used as a field blank.

6.1.3 Sediment

Sediment samples from lakes or sites close to the coast were collected by means of a Kajak sampler. The sediment core was sliced and transferred into pre-heated (400°C) glass jars fitted with aluminium foil lined screw caps and stored in a refrigerator until analysed. A glass jar filled with diatomaceous earth that was exposed to the surrounding environment during the sampling time was used as field blank. Off shore sediments were collected by SGU and sent to the laboratory where they were stored in a freezer (-18°C) until analysis.

The four marine sampling sites (Ö Gotlandsdjupet, Ö Öland, Norrköpingsdjupet, Ö Landsortsdjupet) were chosen from areas with continuous deposition of fine-grained sediment. These sites were identified with hydroacoustic methods (shallow seismic, sub-bottom profiler and chirp side-scan sonar). Prior to sampling, the bottom at the sampling site was inspected with a submarine video camera. Furthermore, a sediment-core from the site was X-rayed with a sediment-scanner (Cato et al. 2000) in order to detect unwanted physical disturbances as strong bioturbation, anchoring, trawling, etc. Sites, which fulfilled the sedimentological demands set up, were then sampled with a Gemini corer and the cores were sliced in vertical position with a core-cutter onboard. Surface sediments (0-1 cm) from four cores taken at each site were mixed in order to neutralise sediment inhomogenities. The samples collected were stored dark and frozen in pre-cleaned and burned glass bottles.

6.1.4 Sludge

The staff at the different treatment plants collected the sludge samples from the anaerobic chambers. The sludge was transferred into pre-heated (400°C) glass jars fitted with aluminium foil lined screw caps and stored at 4°C or -18°C until analysed. A glass jar filled with diatomaceous earth, which was exposed to the surrounding environment during the sampling time, was used as a field blank.

6.1.5 Fish

The fish samples were collected by means of fishing net, hoop net or fishing rod. Samples of herring from background sites were supplied from The Environmental Specimen Bank and the Museum of Natural History (A. Bignert and colleagues). Fish samples were individually wrapped in aluminium foil and stored in a freezer (-20°C).

6.2 Analysis

6.2.1 Chemicals

The solvents (HPLC-quality) acetone, hexane and metyl-*tert*-butylether (MTBE) were delivered from Rathburn (Chemical Ltd., Peeblesshire, Scotland). Solid phase columns containing modified silica sorbent (octadecyl, C18; ethylenediamine-N-propyl, PSA) were delivered from IST (International Sorbent Technology Limited, UK). Sodium sulphate and silica gel was delivered from Merck and pre-heated (400°C) prior to use. All solvents, chemicals and equipment were checked by GC-MS before use. Ultra pure water was produced by a Milli-Q plus equipment (Millipore Corporation, Bedford, MA, USA). Surrogate standards used for quantification of α -, β -endosulfan and endosulfan sulphate were α -D₄-, and β -D₄-endosulfan (Dr Ehrenstorfer, Germany). ¹³C₆-hexachlorobenzene (CIL, MA, USA) was used for quantification of mirex. Octachloronaphtalene, used as volumetric standard was delivered from Dr Ehrenstorfer, Germany.

6.2.2 Extraction

The filter and the sorbent used for air sampling were Soxhlet-extracted with acetone for 24 hours. The acetone was concentrated on a RotoVap (Büchi Switzerland), spiked with surrogate standards and diluted with ultra pure water to a final concentration of 25 % acetone in water. The mixture was extracted with pentane three times. The combined extracts were dried over sodium sulphate, concentrated and fractionated as described below.

The water samples (750 ml) were spiked with surrogate standards and extracted twice with pentane:MTBE (100 + 50 ml). The extracts were combined, dried over sodium sulphate and concentrated with a gentle steam of nitrogen. This extract was subjected for clean up (described below).

Sludge and sediment samples were centrifuged prior to extraction, in order to separate the water from the solid material. Surrogate standards were added and mixed carefully. The sample was extracted with (a) acetone, (b) acetone:MTBE and c) acetone:pentane:MTBE. The pooled extract was diluted with the pore water and ultra pure water to obtain 25 % acetone in water. The extract was mixed carefully. After phase separation the organic extract was safeguarded. The water phase was extracted once more with a mixture of pentane and MTBE. The combined extract was subjected to clean-up prior to GC-MS analysis (described below).

6.2.3 Clean-up of sample extract

Large amounts of natural organic compounds are co-extracted with the analytes. Therefore, an effective clean-up method is needed to obtain a low detection limit. The clean up was performed on two different columns: (a) silica gel and (b) PSA-column.

The silica gel column was made in a Pasteur pipette (5 % deactivated). The sample was dissolved in hexane and added onto the column. Two fractions were collected: F-1 (hexane) containing mirex and F-2 (hexane:MTBE) containing the endosulfans (α - & β -endosulfan and endosulfan sulphate). Fraction F-1 was treated with concentrated sulphuric acid twice (gentle shaking for 30 min) and re-chromatographed on a silica gel (5 %) column using hexane as mobile phase. This fraction was used for quantification of mirex. Fraction F-2 was concentrated and the solvent changed to hexane.

The extract was subjected to clean-up on a PSA-column. Three fractions were collected: F-1' (hexane) containing α -endosulfan, F-2' (hexane:MTBE), which was safeguarded but not analysed and F-3' (hexane:MTBE) containing β -endosulfan and endosulfan sulphate. Fractions F-1' and F-3' were pooled and concentrated and used for quantification of endosulfanes. The fractions F-1 and F-1' + F-3' were spiked with a volumetric standard (octachloronaphthalene) prior to GC-MS analysis.

6.2.4 GC-MS analysis

The extracts were analysed on a 6890 N gas chromatograph coupled to a 5973N mass selective detector (Agilent). The injection was done in pulsed splitless mode at 275°C.

The fused silica capillary column (VF-5MS 30 m x 0.25 mm i.d. x 0.25 μ m film thickness, Varian) was held at 45°C for 1 min, ramped 15°C/min to 200°C and further 5°C/min to 300°C, where it was held for 5 minutes. Helium was used as carrier gas. The mass spectrometer transfer line temperature was 280°C. Data was acquired in selected ion monitoring mode. Electron ionisation at the energy of 70 eV was used for mirex. In order to improve the detection limit most endosulfan extracts were analysed on the same instrument in negative chemical ionisation mode using methane as reagent gas. The characteristic retention times, a quantification ion and one or more supporting ions were used to identify the analytes.

Quantification was based on comparison of peak abundance to the known response of the internal standard (octachloronaphthalene). The reported analyte concentrations were corrected according to the determined surrogate standard losses.

7 Results and discussion

7.1 National

All results are given in Table A 1 and Table A 2 in Appendix .

7.1.1 Mirex

Mirex was not detected in any of the samples in this screening study. The following detection limits were obtained: urban air: 6 pg/m³, deposition: 0.5–1.2 ng/m² day, sediment and sludge: 5–30 ng/g dw and biota: 2–6 ng/g lw. The detection limit for mirex in air from the background stations were due to the sampling technique lower than for urban air samples and varied between 0.3 and 0.4 pg/m³. This is within the same range as the measured concentrations of octachlorostyrene (0.3-0.5 pg/m³ at Råö and 0.4-0.8 pg/m³ at Pallas; Kaj et al., 2005). As a comparison, the concentrations of PCB 153 at Råö during these sampling periods varied between 0.9 and 5 pg/m³ and the concentrations of PBDE 47 between 0.1 and 0.3 pg/m³. Corresponding levels in Pallas were 0.3-0.4 and 0.2-0.6 pg/m³ for PCB 153 and PBDE 47 respectively. Thus, the detection limits for mirex in air obtained in this study were in the same range as detected levels of other POPs. Conclusively, mirex does not show any elevated environmental concentrations in comparison to other POPs.

7.1.2 Endosulfan

7.1.2.1 Background

7.1.2.1.1 Air

α -Endosulfan was detected in all background air samples with slightly higher concentrations at the Swedish West Coast (1.9-17 pg/m³) than in Pallas in northern Finland (2.5-8.6 pg/m³).

Figure 4 shows the measured concentrations in air at the two sites together with the concentrations of α - and γ - hexachlorocyclohexane (HCHs) measured at the same sites during the same period (data from national monitoring of air pollutants). HCHs are pesticides frequently present in air. They are persistent and have global distribution. They are also usually included in sampling programmes, e.g. Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP - www.emep.int).

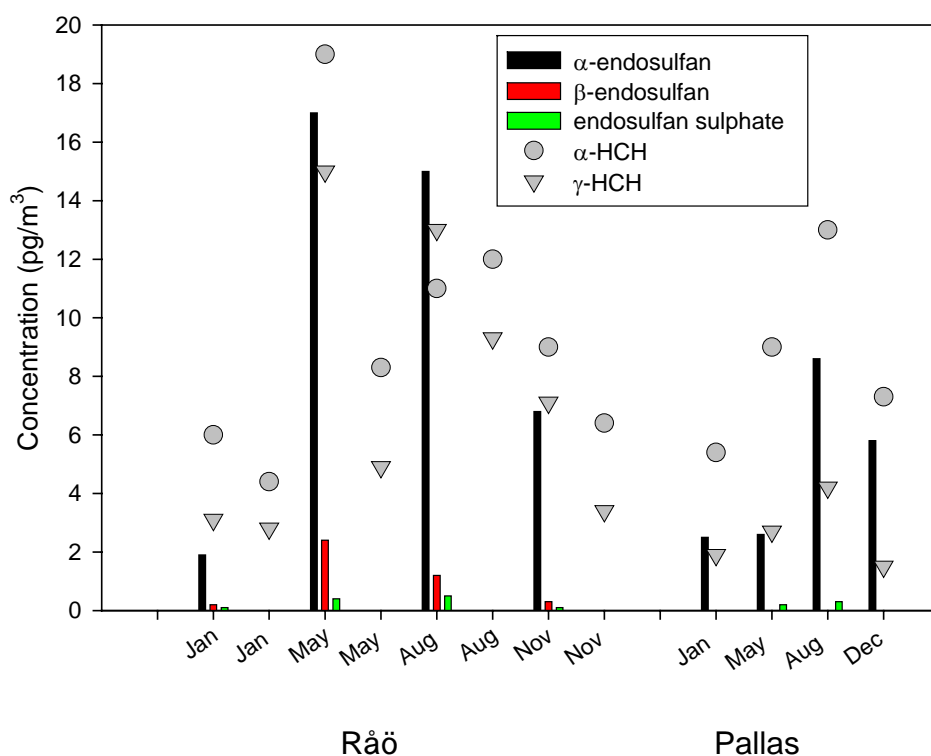


Figure 4. Concentration of α -endosulfan, β -endosulfan and endosulfan sulphate, as compared to the HCH-levels at Råö and Pallas. At Råö, the endosulfan samples were taken over a whole month, whereas the HCH samples are two-week-samples, thus the graph shows two values for HCHs each month, but only one value for endosulfan.

The concentrations of α -endosulfan at Råö were in the same range as both α -HCH and γ -HCH and showed a similar pattern of seasonal variation with higher concentrations during the spring – summer (Figure 4), which may reflect the use of pesticides in central and southern Europe (see chapter 3.2). The concentrations of α -endosulfan at Pallas were lower compared to Råö, especially during the spring and summer period, which is expected as the south of Sweden is closer to source areas than the north of Finland. There was an indication of seasonal variation of α -endosulfan also in Pallas but not as pronounced as in Råö.

The occurrence of α -endosulfan in the Swedish and the sub-Arctic atmosphere indicates that long-range transport from surrounding countries occurs, as there is no approved use within Sweden. This transport seems to follow the pattern of long-range transport of HCHs (Figure 4), which are also banned in Sweden, but still have limited use in other European countries. As mentioned previously, endosulfan was still used in several European countries as late as 1999.

The chemically less stable β -endosulfan was only detected at Råö (0.2-2.4 pg/m^3 , detection limit at Pallas was 0.4 pg/m^3) and concentrations were lower compared to both α -endosulfan and HCHs. A seasonal variation with higher concentrations in the spring-summer was found also for β -endosulfan.

The transformation product endosulfan sulphate, which is more stable than α -endosulfan, was detected in all samples from Råö (0.1-0.5 $\mu\text{g}/\text{m}^3$) and during the summer period also in the samples from Pallas (0.2-0.3 $\mu\text{g}/\text{m}^3$, detection limit: 0.2 $\mu\text{g}/\text{m}^3$). The air concentrations of endosulfan sulphate were like endosulfan slightly higher during the summer compared to the winter period.

The air concentrations of α -endosulfan and β -endosulfan found at the Swedish background sites were somewhat lower or in the same range as concentrations measured in the central Pyrenees and High Tatra (van Drooge et al., 2004). Van Drooge et al. (2004) also observed a positive correlation between concentrations and temperature, which is in good agreement with the findings in the current study, reflecting the seasonal use of endosulfan in European countries. The ratios $\alpha/(\alpha+\beta)$ in the air samples from Råö and Pallas were fairly equal (average 0.91 sd 0.04) and similar to the ratio in technical endosulfan (0.7; van Drooge et al., 2004).

7.1.2.1.2 Deposition

Endosulfan was found in all the deposition samples from the Swedish west coast, but was not detected in deposition in the north of Finland, which is consistent with the observation for air, where lower concentrations were found in Pallas. The deposition fluxes at Råö of α -endosulfan varied between 0.2 and 1.4 $\text{ng}/\text{m}^2\text{day}$, β -endosulfan between 0.1 and 3.3 $\text{ng}/\text{m}^2\text{day}$ and endosulfan sulphate between 0.2 and 0.6 $\text{ng}/\text{m}^2\text{day}$ (Figure 5). The detection limits at Pallas varied between 0.1 and 0.3 $\text{ng}/\text{m}^2\text{day}$.

The deposition fluxes of α -, β and endosulfan sulphate were in the same range as fluxes of HCHs measured at Råö during the same sampling period and show the same fluctuations over the year (Figure 5). The daily deposition of endosulfan at Råö was lower than the measured deposition in the Alps and Pyrenees (6 – 11 $\text{ng}/\text{m}^2\text{day}$ see Table 5).

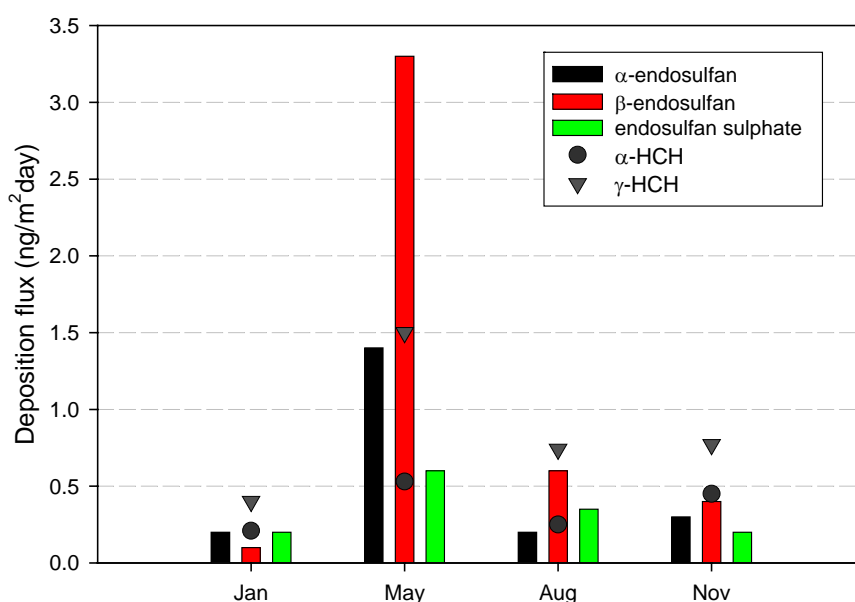


Figure 5. Deposition flux of endosulfan in deposition in Råö as compared with fluxes of HCH measured at the same time period.

In contrast to the air samples, the β -endosulfan isomer generally dominated in deposition, which may be due to the difference in vapour pressure between the isomers. β -endosulfan has a lower vapour pressure than α -endosulfan and is more likely to bind to particles, which will affect the deposition process positively. The proportion of the more stable transformation product endosulfan sulphate, was also higher in the deposition compared to the air, indicating differences in the deposition processes or that transformation of α - and β -endosulfan may take place in the deposition. Figure 6 shows the distribution of the endosulfan components in deposition as compared to the distribution in the atmosphere.

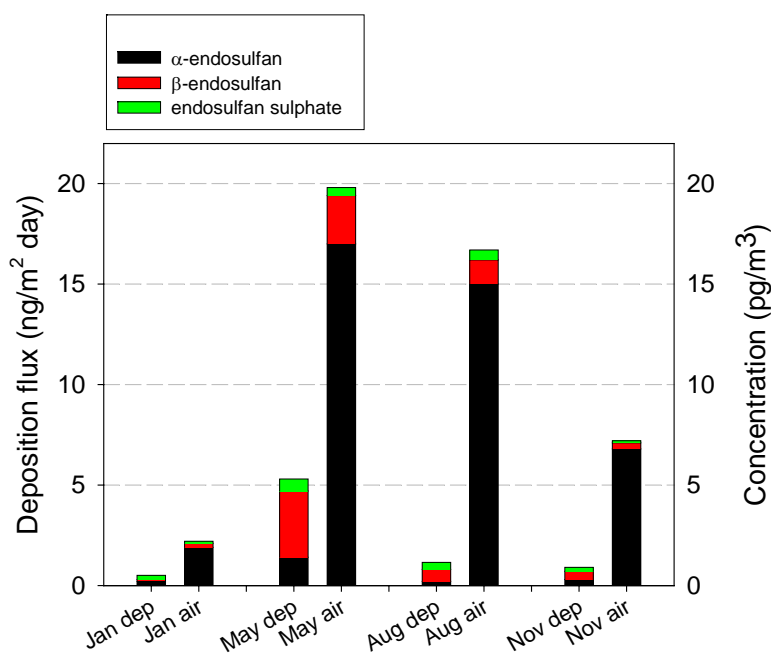


Figure 6. Distribution of α - and β -endosulfan and endosulfan sulphate in deposition as compared to the distribution in air. The left bars represent the deposition, with the y-scale on the left axis, whereas the right bars represent the atmospheric concentration, with the y-scale on the right axis.

The ratio α -/ β - in the deposition samples collected at Råö varied between 0.2 and 0.6. Carrera et al. (2002) observed a ratio α -/ β - of 0.4-0.7 in deposition samples collected in the Alps and Pyrenees. Thus, a higher proportion of β -endosulfan occurs in the deposition in Scandinavia compared to high-altitude sites in the central/south of Europe.

7.1.2.1.3 Sediment

α - and β -endosulfan were not detected in any of the background sediment samples (detection limit: <0.5-1ng/g DW) while the more stable transformation product endosulfan sulphate occurred in concentrations between 0.09 and 0.15 ng/g DW. The partitioning properties of endosulfan indicate that small amounts may partition to sediment, especially when released directly to water (see chapter 2.2). When released to the atmosphere, which would be the case most relevant for Sweden,

the percentage ending up in sediment is predicted to be very low, which is in agreement with the findings in the current study.

The concentrations of endosulfan sulphate in the background sediments were in the same range as other POPs, such as chlordane, HCHs and individual PCBs, for which long range atmospheric transport and deposition is an important pathway for the occurrence in the sediments (Sternbeck et al., 2003).

7.1.2.1.4 Biota

Samples of herring and Baltic herring were used to determine background levels of endosulfan in biota. α - and β -endosulfan were not detected in any of the 6 samples analysed (detection limits 2-6 ng/g lw). Endosulfan sulphate was found in one fish sample from Ängskärsklubb in northern Uppland (7.7 ng/g lw). The results indicate that the transformation product endosulfan sulphate may occur in biota from background sites in Sweden.

7.1.2.2 Urban environment and diffuse sources

α -endosulfan was detected in all three urban air samples (9.9–28 pg/m^3) while β -endosulfan and endosulfan sulphate were detected in only one of the samples in concentrations of 2.8 and 0.79 pg/m^3 respectively. All samples were taken in November/December 2004. The detection limits were higher in the urban air samples (β -: 2 pg/m^3 and endosulfan sulphate: 0.4 pg/m^3) compared to the samples from the background sites, because of the different sampling technique (low volume air sampler). The concentrations of α -endosulfan in urban air were in the same range as those measured at the background stations with the exception of the last sample, which exceeded the others (Figure 7). In this sample, also β -endosulfan and endosulfan sulphate were identified.

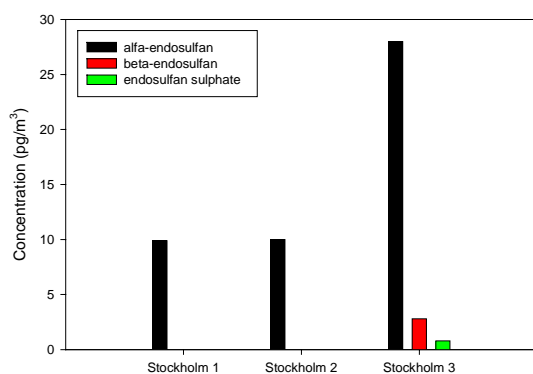


Figure 7. Concentrations of endosulfan in urban air

α -endosulfan was found in two out of three urban deposition samples taken in November and December (fluxes of 0.1 and 0.2 ng/m^2 day, respectively), and in the latter, also endosulfan sulphate was identified (0.1 ng/m^2 day). These fluxes are slightly lower than the observed fluxes on the west coast in november, but in the same range as the detection limits of deposition in Pallas in the same time period.

Endosulfan sulphate was found in lake sediments from the urban surroundings and in sediments from central Stockholm. Concentrations varied between <0.3 and 0.45 ng/g dw (identified in 5 out of 6 samples), which is higher than the concentrations at the background stations (see chapter 7.1.2.1.3). No other endosulfan components were detected in urban sediments. Whether the increased concentrations of endosulfan sulphate in urban sediments are a result of higher deposition in this area, of indirect emissions via storm water and/or STPs or a greater extent of transformation of endosulfan to the sulphate in this area remains unclear.

The concentrations of all compounds in sludge were below the detection limit (7 ng/g dw). Endosulfan sulphate was, however, detected in low concentrations in compost leachate water from Borlänge and Västerås (1.6 and 0.2 ng/L respectively), but not in landfill leachate from Högbytorp (<0.2 ng/L).

The results indicate that long-range transport is of importance also for the occurrence of endosulfan in the urban environment and that local diffuse emissions to air are limited. The importance of diffuse emissions is difficult to estimate from the measurements, but there is an indication of possible emissions of the degradation product via leachate water.

7.2 Regional

Mirex and endosulfan were only analysed in three regional samples, which all showed levels below the detection limits. The detection limits for mirex varied from 1 - 4 ng/g dw, and for endosulfan components in sludge and sewage water 7 ng/g dw and 30 ng/L respectively.

8 Conclusions

Mirex was not detected in any of the samples analysed. However, the detection limits were in the same range as measured concentrations of other pollutants in the area. Conclusively, mirex does not occur in elevated concentrations in the Swedish environment in comparison to other pollutants.

Endosulfan and its transformation product endosulfan sulphate were detected in air in the same concentration range as the HCHs, and with the same seasonal variation. Also the deposition fluxes of endosulfan components were in the same order of magnitude as individual HCHs and followed the same seasonal fluctuations. The similarity between endosulfan and HCH levels and fluctuations was observed at both background stations (Råö at the Swedish West Coast and Pallas in northern Finland).

The concentrations of endosulfan in urban air were similar to those at the background stations, implying low impact of local diffuse emissions to air.

The concentrations of endosulfan in the aquatic systems (i.e. in biota and sediments) were generally below the detection limit. However, the stable transformation product endosulfan sulphate was found in background as well as urban sediments, with higher concentration in the urban sediments. It was also found in one biota sample and in compost leachate water.

Conclusively, endosulfan shows a pattern indicating that it mainly enters the Swedish environment in a similar manner as HCHs, i.e. via long-range atmospheric transport and deposition. The fact that endosulfan sulphate was found in background sediments and biota indicates that atmospheric deposition may result in detectable concentrations in the aquatic environment. Additional analysis of e.g. soils and background surface water would give further information about the impact of atmospheric deposition on the Swedish environment.

Considering the common occurrence in the Swedish atmosphere, the fact that levels are similar to those of other POPs and the indications of long-range transport as the major emission source of endosulfan in Sweden, regular monitoring of endosulfan in air for at least a shorter time period would give useful information about the temporal trends of endosulfan in Swedish air.

Endosulfan sulphate occurred in compost leachate and in urban sediments, the latter showing higher concentrations than corresponding background samples. This may be a sign of possible ongoing diffuse emissions through sewage systems or storm water, which may arise from e.g. consumption of contaminated food followed by degradation to endosulfan sulphate. Further analysis of e.g. outgoing sewage water, sewage sludge, and/or food stuffs would help addressing this issue. Additionally, further measurements of biota samples would provide information about the general occurrence in Swedish biota.

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Appendix

Table A 1. Samples and results from national screening program for mirex

Sample ID	Location	Matrix	Sampling date	X RT 90	Y RT 90	Unit	Mirex	DW (%)
Background								
RA 01-04	Råö	Air	2003-12-29 – 2004-01-26			pg/m ³	<0.3	-
RA 19-22	Råö	Air	2004-05-03 – 2004-06-01			pg/m ³	<0.4	-
RA 33-36	Råö	Air	2004-08-09 – 2004-09-06			pg/m ³	<0.4	-
RA 45-48	Råö	Air	2004-11-01 – 2004-11-29			pg/m ³	<0.3	-
Pallas Jan	Pallas	Air	2004-01-19 – 2004-01-26			pg/m ³	<1	-
Pallas Maj	Pallas	Air	2004-05-24 – 2004-05-31			pg/m ³	<1	-
Pallas Aug	Pallas	Air	2004-08-16 – 2004-08-23			pg/m ³	<1	-
Pallas Dec	Pallas	Air	2004-11-22 – 2004-11-29			pg/m ³	<1	-
RA 01-04	Råö	Deposition	2003-12-29 – 2004-02-02			ng / m ² day	<0.5	-
RA 19-22	Råö	Deposition	2004-04-26 – 2004-06-01			ng / m ² day	<0.5	-
RA 33-36	Råö	Deposition	2004-07-26 – 2004-08-30			ng / m ² day	<0.5	-
RA 45-48	Råö	Deposition	2004-11-03 – 2004-11-29			ng / m ² day	<0.6	-
Pallas Jan	Pallas	Deposition	2004-01-19 – 2004-01-26			ng / m ² day	<0.5	-
Pallas Maj	Pallas	Deposition	2004-05-24 – 2004-05-31			ng / m ² day	<0.5	-
Pallas Aug	Pallas	Deposition	2004-08-16 – 2004-08-23			ng / m ² day	<0.5	-
Pallas Dec	Pallas	Deposition	2004-11-22 – 2004-11-29			ng / m ² day	<0.5	-
MR-3750	Ö Gotlandsdjupet, 0-2 cm 121 m SGU 04-0058	Sediment	Autumn 2004	6216805	1697299	ng/g DW	<3	9.5
MR-3751	Ö Öland, 0-2 cm 77 m SGU 04-0368	Sediment	Autumn 2004	6277308	1607374	ng/g DW	<3	8.3
MR-3752	Norrköpingsdjupet, 0-2 cm 179 m SGU 07i-001	Sediment	Autumn 2004	6435399	1625504	ng/g DW	<4	6.6
MR-3753	Ö Landsortsdjupet, 0-2cm 403 m SGU 09i-0841	Sediment	Autumn 2004	6508995	1648002	ng/g DW	<7	3.8
MR-3559	Stockholm Gälnan, 0-2 cm 24 m depth	Sediment	2004-10-16	6664669	1666854	ng/g DW	<3	18.8
MR-3639	V. Fladen	Herring	2003-09-16	57° 04' 47"	15° 55' 18"	ng/g lipid	<2	

Sample ID	Location	Matrix	Sampling date	X RT 90	Y RT 90	Unit	Mirex	DW (%)
MR-3640	Ångskärsklubb	Baltic herring	2003-10-01	65° 43'	23° 03'	ng/g lipid	<2	
MR-3641	Landsort	Baltic herring	2003-11-12	57° 12' 27"	11° 39' 53"	ng/g lipid	<2	
MR-3642	Utlången	Baltic herring	2003-10-10	58° 17'	17° 50'	ng/g lipid	<6	
MR-3643	Väderöarna	Herring	2003-09-04	58° 43'	10° 51'	ng/g lipid	<2	
MR-3644	Storöfjärden, Kalix skårgård	Baltic herring	2003-09-29	60° 30'	18° 15'	ng/g lipid	<4	
Diffuse sources, STP								
MR-3760	Henriksdal STP	Sludge	2004-11-16			ng/g DW	<18	26.7
MR-3848	Eslöv STP	Sludge	2004-12-07			ng/g DW	<24	18.4
MR-3701	Floda STP	Sludge	2004-11-08			ng/g DW	<19	27.7
Urban								
Stockholm 1	Stockholm, Hudiksvallsgatan 2	Air	2004-11-08 – 2004-11-22			pg/m ³	<6	
Stockholm 2	Stockholm, Hudiksvallsgatan 2	Air	2004-11-22 – 2004-12-06			pg/m ³	<6	
Stockholm 3	Stockholm, Hudiksvallsgatan 2	Air	2004-12-06 – 2004-12-20			pg/m ³	<6	
MR-4012	Stockholm, Hudiksvallsgatan 2	Deposition	2004-11-08 – 2004-12-06			ng / m ² day	<0.7	
MR-4013	Stockholm, Hudiksvallsgatan 2	Deposition	2004-12-06 – 2005-01-03			ng / m ² day	<0.7	
MR-4014	Stockholm, Hudiksvallsgatan 2	Deposition	2005-01-03 – 2005-02-01			ng / m ² day	<1.2	
MR-2535	Stockholm Sicklasjön, 0-2 cm, mixed samples, 4.5 m depth	Sediment	Spring 2002	6577886	1632207	ng/g DW	<20	4.8
MR-2539	Stockholm Laduviken, 0-2 cm, mixed samples, 3 m depth	Sediment	Spring 2002	6584432	1629075	ng/g DW	<30	3.2
MR-2541	Stockholm Drevviken, 0-2 cm, mixed samples, 12 m depth	Sediment	Spring 2002	6570599	1635190	ng/g DW	<20	5.8
MR-2530	Stockholm, Strömmen, 0-2 cm, mixed samples, 27 m depth	Sediment	Spring 2002	6581049	1634496	ng/g DW	<20	5.5
MR-2547	Stockholm, Riddarfjärden, 0-2 cm, mixed samples, 19 m depth	Sediment	Spring 2002	6580116	1627280	ng/g DW	<5	27.8
MR-2549	Stockholm, Fjäderholmarna, 0-2 cm, mixed samples, 28 m depth	Sediment	Spring 2002	6580073	1629454	ng/g DW	<20	6.4

Table A 2. Samples and results from national screening program for endosulfan and endosulfan sulphate

Category	Sample ID	Location	Matrix	Sampling date	Co-ordinates	Unit	α -endo-sulfan	β -endo-sulfan	ES sulphate	DW/LW (%)	
Back-ground	RA 01-04	Råö	Air	2003-12-29 – 2004-01-26	6369857	1266139	1.9	0.2	0.1	-	
	RA 19-22	Råö	Air	2004-05-03 – 2004-06-01	6369857	1266139	17	2.4	0.4	-	
	RA 33-36	Råö	Air	2004-08-09 – 2004-09-06	6369857	1266139	15	1.2	0.5	-	
	RA 45-48	Råö	Air	2004-11-01 – 2004-11-29	6369857	1266139	6.8	0.3	0.1	-	
	Pallas Jan	Pallas	Air	2004-01-19 – 2004-01-26	67° 58'N	24° 07'E	2.5	<0.4	<0.2	-	
	Pallas Maj	Pallas	Air	2004-05-24 – 2004-05-31	67° 58'N	24° 07'E	2.6	<0.4	0.2	-	
	Pallas Aug	Pallas	Air	2004-08-16 – 2004-08-23	67° 58'N	24° 07'E	8.6	<0.4	0.3	-	
	Pallas Dec	Pallas	Air	2004-11-22 – 2004-11-29	67° 58'N	24° 07'E	5.8	<0.4	<0.2	-	
	RA 01-04	Råö	Deposition	2003-12-29 – 2004-02-02	6369857	1266139	0.2	0.1	0.2	-	
	RA 19-22	Råö	Deposition	2004-04-26 – 2004-06-01	6369857	1266139	1.4	3.3	0.60	-	
	RA 33-36	Råö	Deposition	2004-07-26 – 2004-08-30	6369857	1266139	0.2	0.6	0.35	-	
	RA 45-48	Råö	Deposition	2004-11-03 – 2004-11-29	6369857	1266139	0.3	0.4	0.2	-	
	Pallas Jan	Pallas	Deposition	2004-01-19 – 2004-01-26	67° 58'N	24° 07'E	<0.2	<0.1	<0.1	-	
	Pallas Maj	Pallas	Deposition	2004-05-24 – 2004-05-31	67° 58'N	24° 07'E	<0.2	<0.1	<0.1	-	
	Pallas Aug	Pallas	Deposition	2004-08-16 – 2004-08-23	67° 58'N	24° 07'E	<0.3	<0.1	<0.1	-	
	Pallas Dec	Pallas	Deposition	2004-11-22 – 2004-11-29	67° 58'N	24° 07'E	<0.3	<0.1	<0.1	-	
	MR-3750	Ö Gotlandsdjupet, 0-2 cm 121 m SGU 04-0058	Sediment	2004	6216805	1697299	ng/g DW	< 0.5	< 0.5	0.09	9.5
	MR-3751	Ö Öland, 0-2 cm 77 m SGU 04-0368	Sediment	2004	6277308	1607374	ng/g DW	< 0.5	< 0.5	0.09	8.3
	MR-3752	Norrköpingsdjupet, 0-2 cm 179 m SGU 07i-001	Sediment	2004	6435399	1625504	ng/g DW	< 0.5	< 1	0.13	6.6
	MR-3753	Ö Landsortsdjupet, 0-2cm 403 m SGU 09i-0841	Sediment	2004	6508995	1648002	ng/g DW	< 0.5	< 1	0.15	3.8
MR-3559	Stockholm Gälnan, 0-2 cm 24 m depth	Sediment	2004-10-16	6664669	1666854	ng/g DW	< 7	< 7	< 7	18.8	
MR-3639	V. Fladen	Herring	2003-09-16	57° 04' 47"	15° 55' 18"	ng/g lipid	< 3	< 3	< 1	4.5	
MR-3640	Ångsskärsklubb	Baltic herring	2003-10-01	65° 43'	23° 03'	ng/g lipid	< 2	< 2	7.7	4.6	
MR-3641	Landsort	Baltic herring	2003-11-12	57° 12' 27"	11° 39' 53"	ng/g lipid	< 3	< 2	< 2	1.4	

Table A 3 Cont.

Category	Sample ID	Location	Matrix	Sampling date	Co-ordinates	Unit	α -endo-sulfan	β -endo-sulfan	ES sulphate	DW/LW (%)
Back-ground	MR-3642	Utlången	Herring	2003-10-10	55°57' 27" 15°47' 42"	ng/g lipid	<7	<9	<3	1.7
	MR-3643	Väderöarna	Herring	2003-09-04	58°43' 10°51'	ng/g lipid	<2	<2	<1	6.4
	MR-3644	Storöfjärden, Kalix skärgård	Baltic herring	2003-09-29	60° 30' 18°15'	ng/g lipid	<6	-	<46	2.3
Diffuse sources	MR-3760	Henriksdal STP	Sludge	2004-11-16		ng/g DW	<7	<7	<7	26.7
	MR-3848	Esiöv STP	Sludge	2004-12-07		ng/g DW	<7	<7	<7	18.4
Category	Sample ID	Location	Matrix	Sampling date	co-ordinates	Unit	α -endo-sulfan	β -endo-sulfan	ES sulphate	DW/LW (%)
Diffuse sources	MR-3701	Floda STP	Sludge	2004-11-08		ng/g DW	<7	<7	<7	27.7
	MR-3928	Upplands Bro Högbytorp Landfill	Lechate water	2005-02-16		ng/l	<1	<1	<0.2	-
	MR-3758	Borlänge compost	Lechate water	2004-11-16		ng/l	<3	<2	1.6	-
	MR-3691	Västerås compost	Lechate water			ng/l	<3	<2	0.22	-
	Stockholm 1	Stockholm, Hudiksvallsgatan 2	Air	2004-11-08 – 2004-11-22		pg/m ³	9.9	<2	<0.4	-
Stockholm 2	Stockholm, Hudiksvallsgatan 2	Air	2004-11-22 – 2004-12-06		pg/m ³	10	<2	<0.4	-	
Stockholm 3	Stockholm, Hudiksvallsgatan 2	Air	2004-12-06 - 2004-12-20		pg/m ³	28	2.8	0.79	-	
MR-4012	Stockholm, Hudiksvallsgatan 2	Deposition	2004-11-08 – 2004-12-06		ng / m ² day	0.1	<0.1	<0.05	-	
MR-4013	Stockholm, Hudiksvallsgatan 2	Deposition	2004-12-06 – 2005-01-03		ng / m ² day	<0.1	<0.1	<0.05	-	
MR-4014	Stockholm, Hudiksvallsgatan 2	Deposition	2005-01-03 – 2005-02-01		ng / m ² day	0.2	<0.1	0.1	-	
MR-2535	Stockholm Sicklasjön, 0-2 cm, mixed samples, 4.5 m depth	Sediment	Spring 2002	6577886	1632207	ng/g DW	<0.5	<0.5	0.36	4.8
MR-2539	Stockholm Laduviken, 0-2 cm, mixed samples, 3 m depth	Sediment	Spring 2002	6584432	1629075	ng/g DW	<1	<1	<0.3	3.2

Table A 4 Cont.

Category	Sample ID	Location	Matrix	Sampling date	Co-ordinates	Unit	α -endo-sulfan	β -endo-sulfan	ES sulphate	DW/LW (%)	
Urban	MR-2541	Stockholm Drevviken, 0-2 cm, mixed samples, 12 m depth	Sediment	Spring 2002	6570599	1635190	ng/g DW	< 0.5	< 0.5	0.26	5.8
	MR-2530	Stockholm, Strömmen, 0-2 cm, mixed samples, 27 m depth	Sediment	Spring 2002	6581049	1634496	ng/g DW	< 1	< 1	0.43	5.5
	MR-2547	Stockholm, Riddarfjärden, 0-2 cm, mixed samples, 19 m depth	Sediment	Spring 2002	6580116	1627280	ng/g DW	< 0.5	< 0.5	0.30	27.8
	MR-2549	Stockholm, Fjäderholmarna, 0-2 cm, mixed samples, 28 m depth	Sediment	Spring 2002	6580073	1629454	ng/g DW	< 1	< 1	0.45	6.4

Table A 5. Samples and results from regional screening of mirex and endosulfan

County	Site	Matrix	Sampling date	Unit	Mirex	α -endosulfan	β -endosulfan	Endosulfan sulphate	DW %
Kalmar	Mouth of Emån, Oskarshamn	Sediment	2004-10-27	ng/g DW	<1	-	-	-	22.7
Kalmar	Hulingen, Hultsfred	Sediment	2004-11-24	ng/g DW	<3	<7	<7	<7	34.4
Värmland	Kristinehamn STP	Sludge	2004-10-26/28	ng/g DW	<4	<7	<7	<7	29.9
Värmland	Kristinehamn STP	Water effluent		ng/l	-	<30	<30	<30	-