

SWECO Environment
Screening Rapport 2008:1

Screening of biocides and organic halogens

Client

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Sammanfattning

Bakgrund och metoder

Inom ramen för screeningprogrammet 2007 så har SWECO Environment på uppdrag av Naturvårdsverket genomfört mätningar av följande ämnen:

- Tolyfluanid som används som en fungicid vid odling av frukt och blommor, vid betning av frön samt som en biocid i färger och träoljor för exteriört bruk
- Klortalonil som används som en biocid i träimpregneringsprodukter samt (utanför Sverige) i båtbottnfärger.
- Diuron som tidigare har använts som ett viktigt ogräsbekämpningsmedel på banvallar, vägar och dikesrenar. Numera används ämnet endast i vattenbaserade färger och oljor för exteriört bruk.
- Cypermtrin som används för bekämpning av skadeinsekter i skogsbruket samt i villaträdgårdar
- Kathon som används för att bekämpa mikroorganismer i en rad hushållsprodukter såsom schampo, tvålar och hudvårdsprodukter. Kathon används även i industriella rengöringsprodukter samt inom pappersindustrin som ett slembekämpningsmedel. Observera att Kathon egentligen består av två ämnen, 2-metyl-3-isothiazolinone (MI) samt 5-chloro-2-metyl-3-isothiazolinone (CMI).
- Propikonazol som används för att bekämpa påväxt av svamp i färger och träoljor. Ämnet används också som en fungicid inom lantbruket.

Dessa ämnen har mätts i ett flertal matriser i provpunkter som påverkas av olika diffusa källor eller punktkällor. Provtagningen genomfördes nationellt med provpunkter som valdes av Naturvårdsverket och SWECO samt regionalt med provpunkter som valdes av respektive länsstyrelse. Resultaten från den regionala samt den nationella provtagningen samutvärderades.

Projektets målsättning har varit att klargöra de huvudsakliga källorna för dessa ämnen till miljön, kartlägga halterna av dessa ämnen i miljön, samt om ämnena påträffas, översiktligt bedöma huruvida de uppmätta halterna utgöra en risk för hälsa och/eller miljö.

En provtagningsstrategi togs fram som omfattade jord, grundvatten, ytvatten, sediment, dagvatten, sediment från dagvattenbrunnar samt avloppsvatten, slam och utloppsvatten från reningsverk.

De huvudsakliga utsläppskällorna till de ämnen som undersöktes var:

- Plantskolor (tolyfluanid och cypermetrin).
- Anläggningar för beredning eller tillverkning av färg (tolyfluanid, propikonazol, diuron, kathon, cypermetrin).
- Deponier som tar emot byggavfall (tolyfluanid, propikonazol, diuron, kathon, cypermetrin).
- Lantbruk (tolyfluanid och propikonazol).
- Lagringsplatser för behandlat eller målat virke (tolyfluanid, propikonazol, diuron, kathon).
- Jord nedanför nyligen målade fasader (tolyfluanid).
- Bangårdar och banvallar (diuron).
- Båtupställningsplatser (klortalonil).
- Tillfälliga lagringsplatser för timmer (cypermetrin).
- Dagvatten från villaträdgårdar (cypermetrin).
- Reningsverk (Kathon).
- Pappers- och massaindustrier (Kathon).
- Enskilda avlopp (Kathon).

Svenska bakgrundshalter i ytvatten och sediment mättes i referenssjöar. Dessutom mättes bakgrundshalter i jord i anslutning till referenssjöarna.

Slutsatser och rekommendationer

Det tycks inte finnas något samband mellan använda mängder av biocider och deras förekomst i miljön. Kathon används t.ex. i en lång rad produkter och i förhållandevis stora mängder men förekommer inte i något prov i denna studie. I en tysk screeningstudie som nyligen genomförts påträffades kathon endast i ett fåtal prov i inkommande vatten till reningsverk och inte alls i andra matriser (sediment, ytvatten). Diuron däremot, som numera mestadels används i vattenbaserade färger, förekommer i ett antal prover både nära punktkällor och i bakgrandområden. Den troligaste orsaken till dessa skillnader är att Diuron är mycket persistent i miljön medan Kathon bryts ner betydligt lättare.

Endast cypermetrin påträffades (i jord) i halter som eventuellt kan ge effekter. Även om diuron och propikonazol i några enskilda fall påträffades i förhållandevis höga halter i avloppsvatten, slam, dagvatten samt grundvatten så var halterna i jord, sediment och ytvatten långt under möjliga effektnivåer.

Några huvudsakliga slutsatser från denna undersökning är:

- De funna halterna av biocider utgör inte några direkta miljö- eller hälsoproblem.
- Färgindustrier, lagringsplatser för impregnerat virke, deponier samt möjligtvis villaträdgårdar tycks vara de några av de viktigaste källorna för dessa ämnen till miljön
- Cypermetrin kan vara en möjlig kandidat för vidare screening. Dels för att de funna halterna i ytjord när timmerlagringsplatser var nära möjliga effektnivåer och dels för att cypermetrin återfanns i hälften av dagvattenproverna från villaträdgårdar. Vidare screening bör möjligtvis fokusera på användning i villaträdgårdar.
- Kolortalonil och Kathon (CMI och MI) påträffades inte i några prov och det finns således inte något behov av vidare screening av dessa ämnen. Möjligtvis bör nedbrytningsprodukter av Kathon utredas vidare eftersom deras persistens och toxicitet är okänd i nuläget.
- Diuron påträffades nära punktkällor och vid bakgrundssjöar. Möjligtvis finns det ett behov av en begränsad screeningsstudie av biologiska prov för att utröna nuvarande halter i biota samt om halterna ökar eller minskar i biota.
- Tolyfluanid återfanns endast i ett fåtal prov och vidare screening av detta ämne är inte nödvändigt. Däremot behöver Tyska undersökningar av nedbrytningsprodukter av tolyfluanid utvärderas för att bedöma om dessa behöver ingå i screeningsstudier i Sverige.

Summary

Background and methods

Within the screening program of 2007 SWECO Environment has had the assignment from the Swedish Environmental Protection Agency to measure the occurrence of:

- Tolyfluanid which is used as fungicide in fruit and flower cultivations, as a seed disinfectant and as a biocide in paint and wood oil products.
- Chlorothalonil which is used as a biocide in wood preservation products and in boat paints.
- Diuron which has been commonly used as a weed killer on railway embankments, roads and parking lots. Today the substance is used as a biocide in water based paints and (outside of Sweden) in boat paints.
- Cypermethrin which is used as an insecticide in forestry and for household applications to control arthropods.
- Kathon which is used as a preservative for the control of microorganisms in aqueous-based industrial products such as cleaning agents and in cosmetics, toiletries and household products such as shampoos, other hair and skin care products, fabric softeners or polishes. Kathon is also widely used as a slemicide in the pulp and paper industry.
- Propiconazole which is used as a fungicide in paint and wood oil products for exterior use to prevent the forming of mould during storage and underneath the painted surface. It is also used in cereal crops and grass seed cultivations.

These substances were measured in various matrices affected by different activities and in background areas in Sweden. The sampling was performed on a national level with sampling points chosen by SWECO and on a regional level with sampling points chosen by regional county boards. Results from the national and the regional screening were collectively evaluated.

The objectives of the project were to elucidate the main sources of these substances to the environment, to elucidate the levels of these substances in the environment and if the substances are found briefly assess whether the levels constitute an environmental and/or health problem.

A national sampling strategy was devised which included soil, groundwater, surface water, sediments, storm water, sediments from storm water manholes as well as incoming water, sludge and effluents from sewage treatment plants.

The major sources to the environment of the investigated substances were:

- Forest seedling nurseries (tolylfluanid, cypermethrin).
- Paint manufacturing industries.
- Landfills receiving painted and impregnated building material (tolylfluanid, propikonazol, diuron, kathon, cypermethrin).
- Agriculture (tolylfluanid, propiconazole).
- Sites where painted and/or impregnated wood is stored (tolylfluanid, propikonazol, diuron, kathon)
- Soils below outdoor building surfaces that had been recently painted (tolylfluanid)
- Railway yards and railway embankments where diuron has been used as a weed killer.
- Marinas (chlorthalonil)
- Intermittent storage sites for timber (cypermethrin)
- Storm water from detached houses and villa gardens (cypermethrin)
- Waste water treatment plants (Kathon)
- Pulp and paper industries (Kathon)
- Single house sewage plants (Kathon)

Swedish environmental background levels in surface water and sediments were determined in reference lakes and in soil in the vicinity of these lakes.

Conclusions and recommendations

There does not seem to be a relation between the amounts of biocides used and the occurrence in the environment. This is exemplified by Kathon that is used in a large number of products but was never found in any sample. Diuron on the other hand is used in smaller amounts, in a few products, but was found at background lakes and in a number of samples at point sources, such as paint factories.

Only Cypermethrin was found at levels (in soil) that could cause any immediate effects. On a few occasions diuron and propiconazole were found at high levels (relative to effect concentrations) in incoming water, storm water, ground water and sludge. However, they were well below any effect levels in surface water, soils and sediments.

Some main conclusions and recommendations are:

- The screened biocides are not found at levels that give rise to any immediate environmental and/or health concern.

- Paint industries, storage sites for treated wood and/or landfills seem to be the most important sources of propiconazole, diuron and tolylfluanid to the environment.
- Cypermethrin is a possible candidate for further screening. The substance was detected in storm water from areas with detached houses and in the topsoil at sites where timber is stored. Further screening should focus on the usage of cypermethrin in pesticides for villa gardens and for protection of felled timber.
- Chlorothalonil and the kathon substances CMI and MI were not detected in any samples. There is no further need for screening of these substances. However, the need for screening of kathon biodegradation products can not be excluded since the stability and ecotoxicity of these compounds is largely unknown.
- It may be pertinent to review German screening studies on the occurrence of degradation products of tolylfluanid before deciding if these should be investigated in the future.

1 Introduction

1.1 Background

At present there is a lack of knowledge regarding the emission, distribution and exposure for many of the chemicals emitted to the environment. The aim of the screening program financed by the Swedish Environmental Protection Agency (Swedish EPA) is to alleviate this lack of knowledge by estimating the occurrence of different chemicals in the environment in relevant matrices (soil, water etc.).

To maximize the information gained from the screening program, measurements are made in many matrices at many sites, but with few samples per site.

The Swedish EPA is responsible for the screening at the national level and selects the chemicals that are to be included. The regional county boards have the option to complement and extend the sampling program by choosing additional sampling point that are of regional interest.

Within the screening program of 2007, SWECO Environment has had the assignment from the Swedish EPA to measure the occurrence of the following biocides and organic halogens:

- tolylfluanide
- chlorothalonil
- diuron
- cypermethrin
- propiconazole
- kathon

All of these substances are used as biocides either directly (in agricultural applications) or in products. Consequently they are all designated as biocides in the following text.

1.2 Objectives

The objectives of the project were to:

- To elucidate the main sources of these substances to the environment.
- To elucidate the levels of these substances in the environment.

- If the substances are found, briefly assess whether the levels constitutes an environmental problem.

1.3 Substance information

1.3.1 Tolyfluanid

Tolyfluanid is used as a fungicide in fruit and flower cultivations and as a seed disinfectant. The Swedish Chemical Agency has recently (2007) revoked all permits for the usage of tolyfluanid in agriculture. The reason is the discovery of a previously unknown degradation product (dimethylsulfamide) which in turn can form nitrosamines when drinking water is treated with ozone. Nitrosamines are known carcinogenics and German authorities have found dimethylsulfamide in both surface water and groundwater.

Tolyfluanid is also a very common fungicide in a number of paint and wood oil products to prevent the forming of mould during storage and underneath the painted surface.

The registered¹ amounts of tolyfluanid in Sweden from the year 1993 – 2005 are presented in figure 1.1 below. Physiochemical and (eco)toxicological properties are presented in table 1.1.

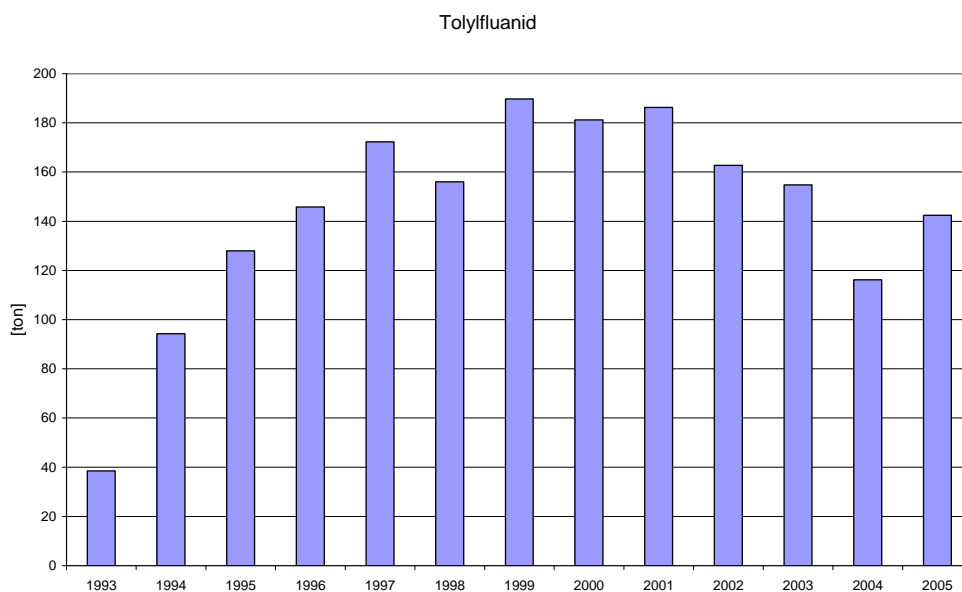
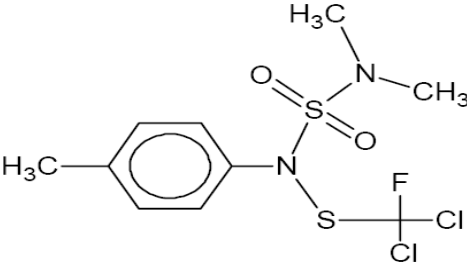


Figure 1.1 Registered amounts of tolyfluanid in Sweden from the year 1993 – 2005

¹The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

Table 1.1 Physiochemical and (Eco)toxicological properties. Source: SWECO (2006)

Common name	Tolyfluanid			
				
Name	Methanesulfenamide, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl)-			
CAS #	731-27-1			
Classification	T; R23 Xn; R48/20 Xi; R36/37/38 R43 N; R50-53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	0.9		mg/l
	Water – organic carbon partition coefficient (K_{oc})	1728	3200	
	Henry's constant	$8 \cdot 10^{-7}$		$\text{atm} \cdot \text{m}^3/\text{mol}$
	Vapor pressure	$2 \cdot 10^{-6}$		mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	0.045	23	mg/l
	NOEC och LOEC	0.0031	0.032	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	1000	1000	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	Oral LD ₅₀ = 250 – 5000 mg/kg. Dermal LD ₅₀ = 500 – 5000 mg/kg.			
PBT classification	P b T			
Theoretical reduction in waste treatment plants	26 %			
Theoretical environmental partitioning	air – 2.46 % , water – 81.3 % , soil – 12.4 % , sediment – 3.89 %			
Guideline values	Swedish surface waters ¹ : 0.2 µg/l			

¹ The Swedish Chemicals Agency has developed guideline values for pesticides in surface waters. The guideline values represent the highest concentration where no negative ecological effects are expected. These values are not binding and are only meant to assist the interpretation of results from environmental monitoring.

1.3.2 Chlorothalonil

Chlorothalonil is used as a biocide in wood preservation products and, in other countries, boat paints (Piedral et al. 2000, Vasilios et al. 2002). Previously it was used as a fungicide in agriculture, mainly in greenhouse growing of cucumbers. Due to its known carcinogenic effects its use in agriculture has been revoked. The usage of a number of paint products containing chlorothalonil has also been revoked by the Swedish Chemical Agency. If a paint or wood preservation product contains very low concentrations of chlorothalonil there is no requirement to reveal the occurrence in a safety data sheet. Consequently, it is difficult to elucidate the precise products that contain this substance.

The registered² amounts of chlorothalonil in Sweden from the year 1994– 2005 are presented in figure 1.2 below. Physiochemical and (eco)toxicological properties are presented in table 1.2

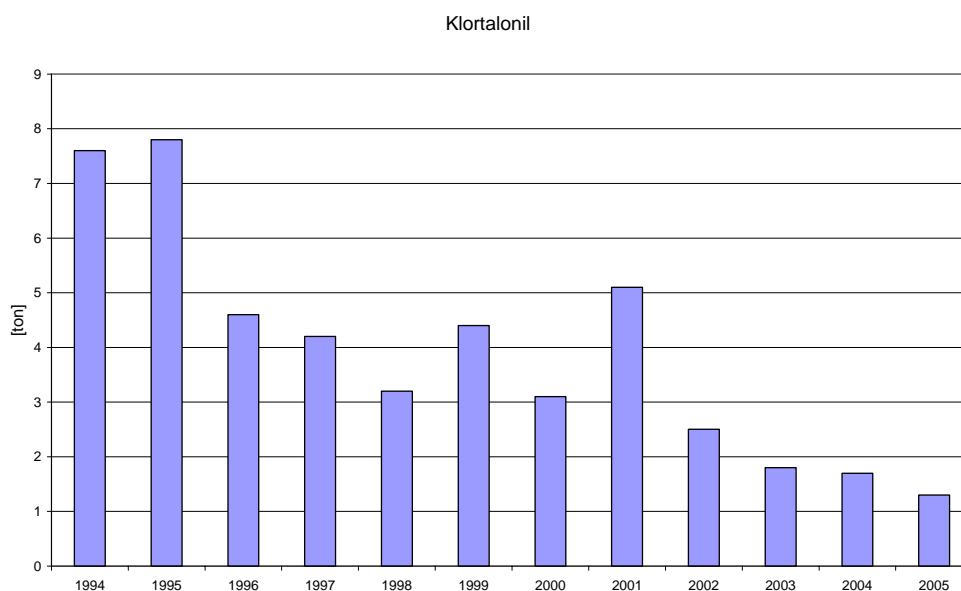
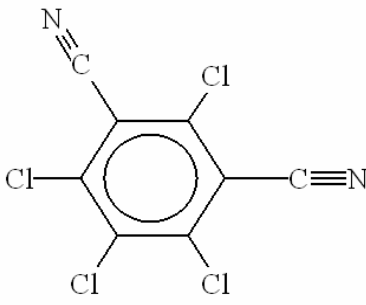


Figure 1.2 Registered amounts of chlorothalonil in Sweden from the year 1994 – 2005

² The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

Table 1.2 Physicochemical and (Eco)toxicological properties of chlorothalonil. Source: SWECO (2006)

Common name	Chlorothalonil			
				
Name	2,4,5,6-tetrachlorobenzene-1,3-dicarbonitrile			
CAS #	1897-45-6			
Classification	Carc. Cat. 3; R40 T+; R26 Xi; R41 Xi; R37 R43 N; R50-53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	0.6	0.96	mg/l
	Water – organic carbon partition coefficient (K_{oc})	1800	2392	
	Henry's constant	$2 \cdot 10^{-7}$	$2 \cdot 10^{-6}$	atm \cdot m ³ /mol
	Vapor pressure	$5.7 \cdot 10^{-5}$	0.098	mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	0.0076	0.17	mg/l
	NOEC och LOEC	-	-	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	650	10 000	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	LD ₅₀ = 2.5 – 3700 mg/kg			
PBT classification	P+ b T			
Theoretical reduction in waste treatment plants	6.2 %			
Theoretical environmental partitioning	<u>air</u> – 5.45 %, <u>water</u> – 13.15 %, <u>soil</u> – 81.35 %, <u>sediment</u> – 0.077 %			
Guideline values	None found			

1.3.3 Diuron

Diuron has commonly been used as a weed killer on railway embankments, roads, parking lots etc. This usage is now discontinued and its main usage has been as a biocide in water based paints for exterior use and boat paints. It has also been used as a biocide in glues and lacquers used in the engineering industries.

The registered³ amounts of diuron in Sweden from the year 1992 – 2005 are presented in figure 1.3 below. Physiochemical and (eco)toxicological properties are presented in table 1.3.

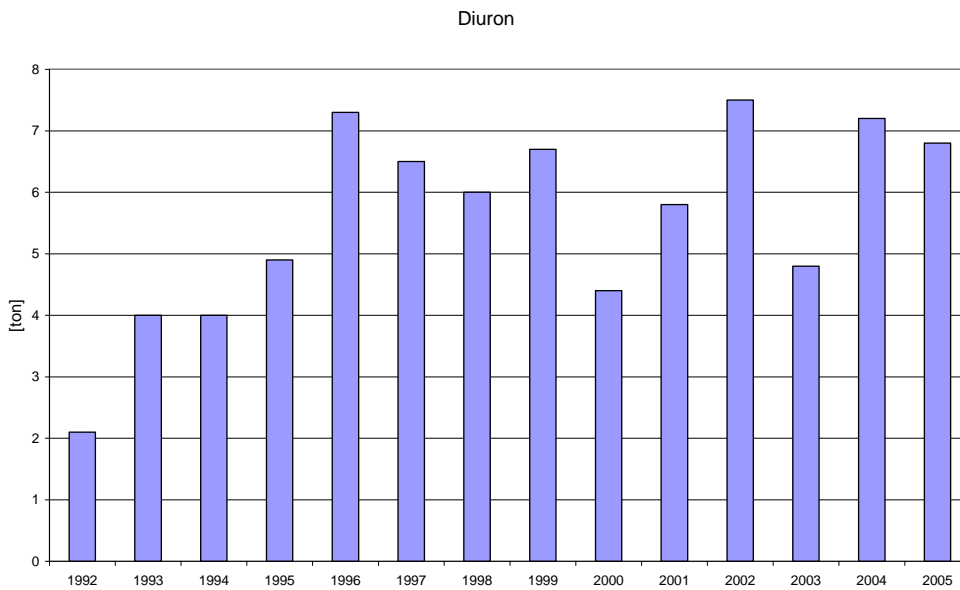
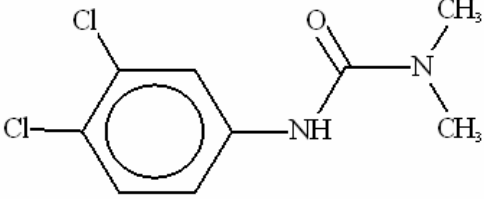


Figure 1.3 Registered amounts of diuron in Sweden from the year 1992 – 2005

³ The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

Table 1.3 Physiochemical and (Eco)toxicological properties of Diuron. Source: SWECO (2006)

Common name	Diuron			
				
Name	3-(3,4-dichlorophenyl)-1,1-dimethyl-urea			
CAS #	330-54-1			
Classification	Carc.3; R40 Xn; R22-48/22 N; R50-53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	35	42	mg/l
	Water – organic carbon partition coefficient (K_{oc})	72	383	
	Henry's constant	$5.04 \cdot 10^{-10}$	$5.8 \cdot 10^{-10}$	Atm \cdot m ³ /mol
	Vapor pressure	$1.7 \cdot 10^{-10}$	$6.9 \cdot 10^{-8}$	mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	0.0013	0.04	mg/l
	NOEC och LOEC	0.005	1	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	1000	5000	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	LD ₅₀ 500 – 1017 mg/kg			
PBT classification	P b T			
Theoretical reduction in waste treatment plants	3.7 %			
Theoretical environmental partitioning	<u>air</u> – 0.00367 %, <u>water</u> – 14.5 %, <u>soil</u> – 85.5 %, <u>sediment</u> – 0.0521 %			
Guideline values	Environmental Quality Standard for one sampling per year ¹ AA-EQS: 0.2 µg/L			

¹ According to the EU Water Framework Directive

1.3.4 Cypermethrin

Cypermethrin is used as an insecticide mainly in forestry to control outbreaks of arthropods. It is used both during planting of saplings and when felled trees are kept at intermittent sites before transport to lumber industries or paper mills. The usage in forestry in Sweden has increased due to major storms in 2005 and 2006 which felled a very large number of trees that had to be intermittently stored.

Cypermethrin is also commonly used in products used to combat and control ants in gardens and inside buildings.

The registered amounts⁴ of cypermethrin in Sweden from the year 1993 – 2005 are presented in figure 1.4 below. Physicochemical and (eco)toxicological properties are presented in table 1.4

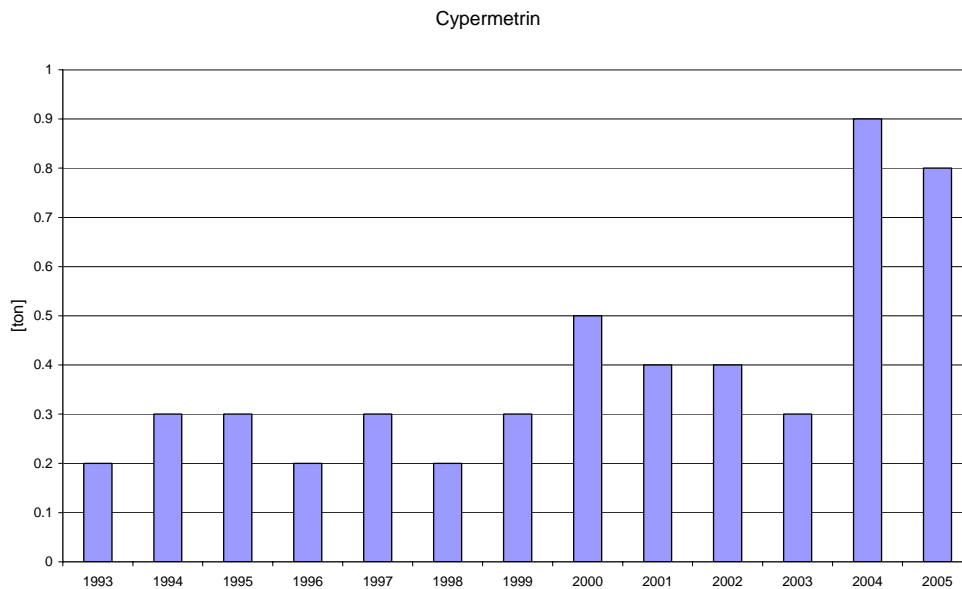
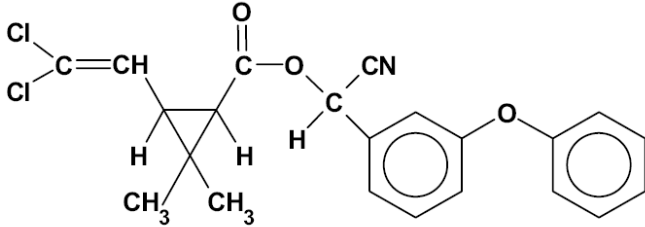


Figure 1.4 Registered amounts of cypermethrin in Sweden from the year 1992 – 2005

⁴ The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

Table 1.4 Physicochemical and (Eco)toxicological properties of Cypermethrin. Source: SWECO (2006)

Common name	Cypermethrin			
				
Name	[cyano-(3-phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate			
CAS #	52315-07-8			
Classification	EU: R: 22-37/38-43-50/53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	0.004	-	mg/l
	Water – organic carbon partition coefficient (K_{oc})	5800	1.6E05	
	Henry's constant	$4.2 \cdot 10^{-7}$	-	Atm \cdot m ³ /mol
	Vapor pressure	$3.1 \cdot 10^{-9}$	$1.7 \cdot 10^{-7}$	mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	$5 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	mg/l
	NOEC och LOEC	$1 \cdot 10^{-5}$	0.0011	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	2634	3951	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	LD ₅₀ 24.6 – 400 mg/kg			
PBT classification	P+ b T+			
Theoretical reduction in waste treatment plants	92.39 %			
Theoretical environmental partitioning	air – 0.199 %, water – 12.6 %, soil – 26.05 %, sediment – 61.15 %			
Guideline values	Swedish surface waters ¹ : 0.0001 - 0.0002 µg/l MPC soil ² : 0.39 mg/kg			

¹ The Swedish Chemicals Agency has developed guideline values for pesticides in surface waters. The guideline values represent the highest concentration where no negative ecological effects are expected. These values are not binding and are only meant to assist the interpretation of results from environmental monitoring.

² Dutch guideline concentration that supposedly protects 95% of all species in a soil. Based on statistical extrapolations or the use of safety factors applied on ecotoxicological data (RIVM 1997).

1.3.5 Kathon

Kathon is a trademark for a group of biocides that consists of a mix of several (isothiazolon-) compounds.

The present study focuses on Kathon GC (CAS No. 55965-84-9) which is one of the most common kathon mixtures containing 2-methyl-3-isothiazolinone (MI) and 5-chloro-2-methyl-3-isothiazolinone (CMI).

These isothiazolinones are mainly used as preservatives for the control of microorganisms (fungi and bacteria) in aqueous-based industrial products such as cleaning agents and in cosmetics, toiletries and household products such as shampoos, other hair and skin care products, fabric softeners or polishes (Madsen et al. 2001, Rafoth et al. 2007). They are also widely used as slemicides in pulp and paper industries.

The cosmetic industry employs a 3:1 CMI/MI mixture as Kathon. In cosmetic products the maximum allowed concentration is 15 ppm of the mixture of MI and CMI (Directive 97/18/EC and Directive 98/16/EC). The products may include water at levels more than 75% and various kinds of salts, e.g. magnesium salts. Examples of commercial products are Kathon CG (cosmetic grade): 0.35% MI and 1.15% CMI = 1.5% active ingredients + magnesium salts, and Kathon 886: 3.8% MI and 10.1% CMI = 13.9% active ingredients.

The registered amounts⁵ of kathon in Sweden from the year 1993 – 2005 are presented in figure 1.5 below. Physiochemical and Ecotoxicological properties are presented in table 1.5.

⁵ The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

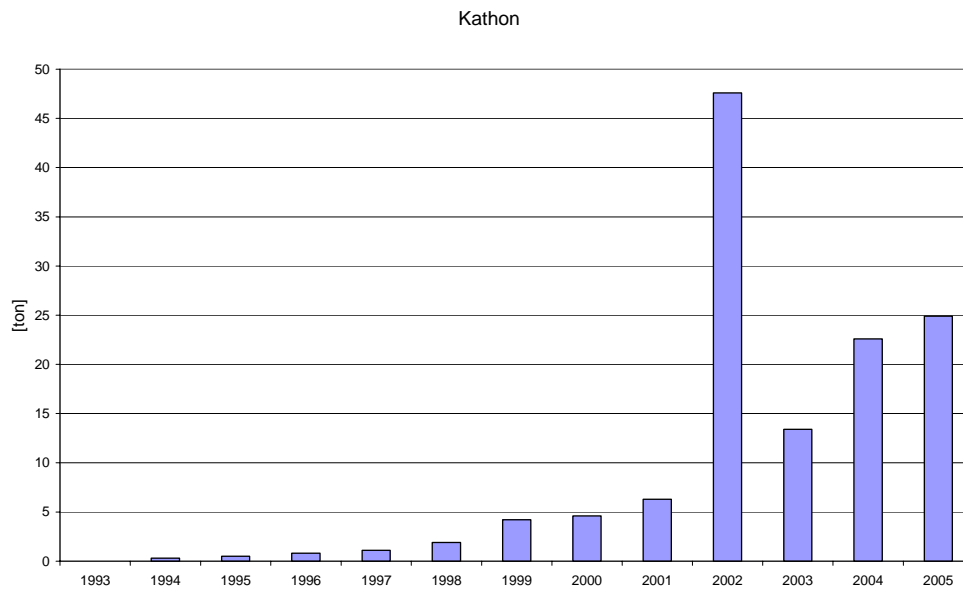
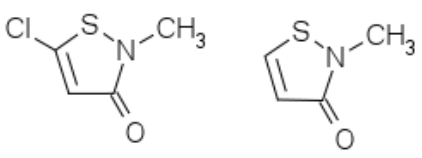


Figure 1.5 Registered amounts of kathon in Sweden from the year 1993 – 2005

Table 1.5 Physiochemical and (Eco)toxicological properties of Kathon. Source: SWECO (2006)

Common name	Kathon			
<i>3:1 mixture</i>				
				
Name	5-chloro-2-methyl-2 H -isothiazol-3-one (CMI) 2-methyl-2 H -isothiazol-3-one (MI)			
CAS #	55965-84-9 (mixture) 26172-55-4; 2682-20-4			
Classification	T; R23/24/25 C; R34 R43 N; R50-53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	235 650	536 700	mg/l
	Water – organic carbon partition coefficient (K _{oc})	27.88	45.15	
	Henrys constant	2.14*10 ⁻⁸	2.92*10 ⁻⁸	atm*m ³ /mol
	Vapor pressure	0.0054	0.031	mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	-	-	mg/l
	NOEC och LOEC	16.5	166	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	-	-	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	LD ₅₀ 53 – 60 mg/kg			
PBT classification	p b T			
Theoretical reduction in waste treatment plants	1.85 %			
Theoretical environmental partitioning	<u>air</u> – 0.116 %, <u>water</u> – 65.9 %, <u>soil</u> – 33.9 %, <u>sediment</u> – 0.0393 %			
Guideline values	=			

1.3.6 Propiconazole

Propiconazole is a fungicide used for example in cereal crops and grass seed cultivations. It is also used as a fungicide at golf courses. Within this project a number of green keepers at golf courses were interviewed. From the interviews it appears that this usage is very rare in Sweden.

Furthermore, propiconazole is a common fungicide in a number of paint and wood oil products for exterior use. Its function is to prevent the forming of mould during storage and underneath the painted surface.

The registered amounts⁶ of propiconazole in Sweden from the year 1992 – 2005 are presented in figure 1.6 below. Physiochemical and (Eco)toxicological properties are presented in table 1.6

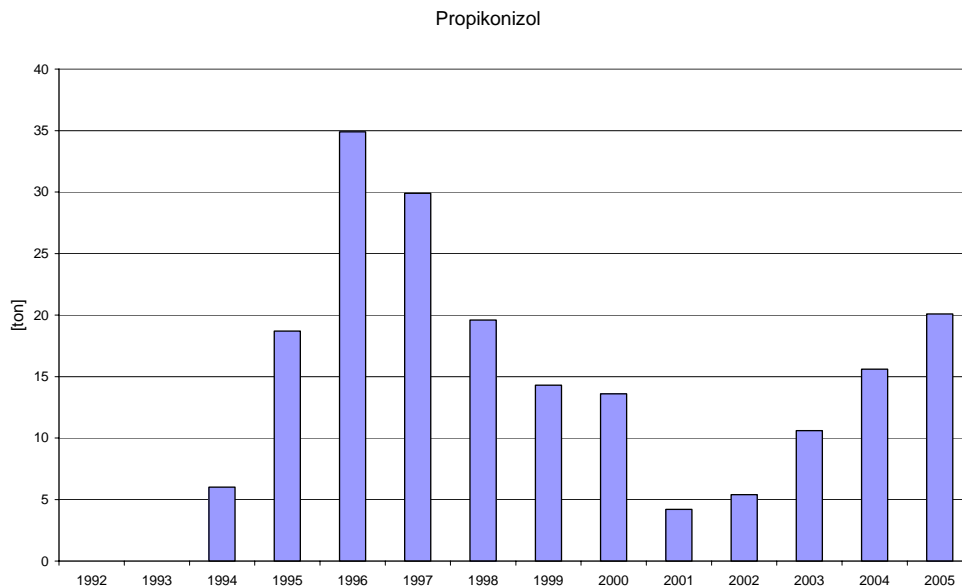
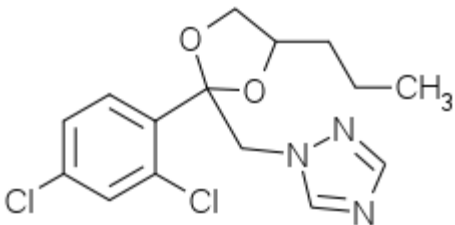


Figure 1.6 Registered amounts of Propiconazole in Sweden from the year 1992 – 2005

⁶ The statistics are based on the amount of pure substance or substance in products that companies have filed to the Swedish Chemicals Agency.

Table 1.6 Physicochemical and (Eco)toxicological properties of Propiconazole. Source: SWECO (2006)

Common name	Propiconazole			
				
Name	1-((2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole			
CAS #	60207-90-1			
Classification	Xn; R22 R43 N; R50-53			
		Min	Max	Unit
Physical and chemical properties	Water solubility	100	110	mg/l
	Water – organic carbon partition coefficient (K_{oc})	1 900	5 564	
	Henry's constant	$4.1 \cdot 10^{-9}$	$4.12 \cdot 10^{-9}$	$\text{atm} \cdot \text{m}^3/\text{mol}$
	Vapor pressure	$1 \cdot 10^{-6}$	-	mmHg
Aquatic ecotoxicology	LC ₅₀ and EC ₅₀	$7 \cdot 10^{-4}$	0.72	mg/l
	NOEC och LOEC	0.5	3	mg/l
Terrestrial ecotoxicology	LC ₅₀ and EC ₅₀	5 620	-	mg/kg soil
	NOEC and LOEC	-	-	mg/kg soil
Toxicology (vertebrates, mostly rats and mice).	LD ₅₀ 1 517 – 4 000 mg/kg			
PBT classification	P b T			
Theoretical reduction in waste treatment plants	19.08 %			
Theoretical environmental partitioning	<u>air</u> – 0.0607 %, <u>water</u> – 8.65 %, <u>soil</u> – 91.1 %, <u>sediment</u> – 0.207 %			
Guideline values	Swedish surface waters ¹ : 7 µg/l			

¹ The Swedish Chemicals Agency has developed guideline values for pesticides in surface waters. The guideline values represent the highest concentration where no negative ecological effects are expected. These values are not binding and are only meant to assist the interpretation of results from environmental monitoring.

2 Methodology

2.1 Sampling Strategy

A national sampling strategy was devised based on two objectives:

- Elucidate the main sources of these substances to the environment
- Elucidate the levels of these substances in the environment

The different matrices chosen and the specific sampling strategy for each substance are presented in the following sections. Environmental background levels in surface water, fish (diuron only) and sediments were determined in samples from regional background reference lakes where the influence from human activities are considered to be minimal in a regional context; Abiskojaure in the northernmost part of Sweden, Ljusacksen in the middle part of Sweden and Krageholmsjön in the southernmost part of Sweden (Figure 2.1).

Soil was also sampled from the areas around these lakes.



Figure 2.1 Background sampling stations

2.1.1 Tolyfluamid

The most important sampling within the national screening were:

Forest seedling nurseries where the substance was used until 2006/2007. Samples were taken both in soil and in drainage water.

Paint industries where the substance is still used as a biocide. Two smaller paint industries and one very large was included. Samples were taken in soil, sludge from an on-site treatment plant (the larger industry), incoming water to the treatment plant, storm water, ground water and sediments.

Landfills receiving painted and impregnated building material. Three large landfills in southern Sweden were included in the study and samples were also taken in

surface waters and sediments influenced by the landfills and in storm water within the landfill.

Agriculture where the substance has been used as a fungicide. Soil, ground water, surface water, and sediments were sampled.

Storage sites where painted and/or impregnated wood is stored outdoors. Samples were mostly taken in storm water and storm water sediments.

Soils below outdoor building surfaces that had been painted with a paint product that contained 0.2% of tolylfluanid. This was to test whether tolylfluanid leached from these surfaces to the soil below.

Originally, foodstuffs (vegetables) were included in the sampling plan. The extent of this sampling was reduced since this substance is measured routinely in vegetables by the Swedish National Food Administration. Also, the number of sites for sampling where small boats are stored during winter (marinas) were reduced since a literature survey revealed that no boat paints on the Swedish market contain this substance.

Within the regional screening programme, this substance was mostly measured at water treatment plants.

The sampling plan and the measured matrices are shown in table 2.1.

Table 2.1 Sampling matrices and the types of sources for tolylfluanid. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programme.

Sampling matrices Tolyfluanid										
Sources	Soil	Sludge	Incoming water	Out-going water	Surface water	Storm water	Landfill leachate	Groundwater	Sediment	Foodstuff
Background	3 / 0				2 / 0				3 / 0	
Diffuse sources					1 / 1				1 / 0	
Waste water treatment plants		3 / 1	1 / 1	3 / 2						
At a locations influenced by the following sources										
a. Waste water treatment plants					2 / 2				1 / 0	
b. Paint industry	1 / 0	1 / 0	1 / 0			4 / 0		2 / 0	3 / 0	
c. Harbours	1 / 0							1 / 0		
d. Agriculture	2 / 0				2 / 0			2 / 0	2 / 0	4 / 0
e. Landfills					1 / 0		11 / 2		1 / 0	
f. Painted surfaces, outdoors	8 / 0									
g. Forest seedling nurseries	6 / 0					1 / 0		1 / 0		
h. Storage sites for impregnated wood	2 / 0					1 / 0			5 / 0	
Total	23 / 0	4 / 1	2 / 1	3 / 2	7 / 3	6 / 0	11 / 2	6 / 0	15 / 0	4 / 0
Grand total	80 / 9									

2.1.2 Chlorothalonil

The most important sampling within the national screening were:

Paint industries where chlorothalonil was previously used. Two smaller paint industries and one very large was included. Samples were taken in soil, sludge from an on-site treatment plant (the larger industry), incoming water to the treatment plant, storm water, groundwater and sediments.

Landfills receiving painted and impregnated building material. Three large landfills in southern Sweden were included in the study and samples were taken in surface waters and sediments influenced by the landfills and in run-off water within the landfill.

Storage sites where painted and/or impregnated wood is stored outdoors. Samples were mostly taken in storm water and storm water sediments.

Marinas where boats are kept at land during winter. Chlorothalonil is used in boat paint that can be bought outside of Sweden. Also, when testing a number of environmentally friendly boat paints used on the western coast of Sweden, it was found that one contained 10% chlorothalonil without any information on the paint label⁷.

The regional sampling of chlorothalonil was sparse and focused mostly on sewage treatment plants.

The sampling plan and the measured matrices is shown in table 2.2

Table 2.2 Sampling matrices and the types of sources for chlorothalonil. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programme.

Sampling matrices chlorothalonil									
Sources	Soil	Sludge	Incoming water	Outgoing water	Surface water	Storm water	Landfill leachate	Ground-water	Sediment
Background	3 / 0				2 / 1				3 / 0
Diffuse sources					1 / 2				1 / 0
Waste water treatment plants		3 / 1	1 / 1	3 / 2					
At a locations influenced by the following sources									
a. Waste water treatment plants					1 / 2				1 / 0
b. Paint industries		1 / 0	1 / 0			3 / 0		2 / 0	3 / 0
c. Harbors / boat storage sites	2 / 0							1 / 0	
d. Agriculture	2 / 0				2 / 0			2 / 0	2 / 0
e. Landfills					1 / 0		11 / 2		1 / 0
f. Forest seedling nurseries								1 / 0	
g. Storage sites for treated wood	2 / 0					1 / 0			4 / 0
Total	7 / 0	4 / 1	2 / 1	3 / 2	7 / 5	4 / 0	11 / 2	6 / 0	15 / 0
Grand total	<u>59 / 11</u>								

⁷ Mindre Gift på Drift. Länsstyrelsen Västra Götaland Rapport nr 1999:37. Rapport från Kemikalieprojektet inom ramen för Skärgårdsuppdraget.

2.1.3 Diuron

The most important sampling within the national screening were:

Paint industries where the substance is still used as a biocide. Two smaller paint industries and one very large was included. Samples were taken in soil, sludge from an on site treatment plant (the larger industry), incoming water to the treatment plant, storm water, ground water and sediments

Landfills receiving painted and impregnated building material. Three large landfills in southern Sweden were included in the study and samples were taken in surface waters and sediments influenced by the landfills and in storm water within the landfill.

Storage sites where painted and/or impregnated wood is stored outdoors. Samples were mostly taken in storm water and storm water sediments.

Railway yards and railway embankments where diuron has been used as a weed killer.

The regional sampling of chlorothalonil was sparse and focused mostly on water treatment plants.

The sampling plan and the measured matrices is shown in table 2.3

Table 2.3 Sampling matrices and the types of sources for diuron. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programmes.

Sampling matrices Diuron										
Sources	Soil	Sludge	Incoming water	Outgoing water	Surface water	Storm water	Landfill leachate	Ground-water	Fish	Sediment
Background	3 / 0				1 / 1				3/0	3 / 0
Diffuse sources										
Waste water treatment plants		2 / 3	1 / 1	1 / 3						
At a locations influenced by the following sources										
a. Waste treatment plants					1 / 1					1 / 0
b. Paint industries		1 / 0	1 / 0			3 / 0		2 / 0		
c. Harbors / boat storage sites	3 / 0							1 / 0		6 / 0
d. Railway yards / embankments					2 / 0			6 / 0		1 / 0
e. Landfills						3/0	6 / 0			
g. Storage sites for treated wood	2 / 0					1 / 0				4 / 0
Total	8 / 0	3 / 3	2 / 1	1 / 3	4 / 2	7 / 0	6 / 0	9 / 0	3/0	15 / 0
Grand total	<u>57 / 9</u>									

2.1.4 Cypermethrin

The most important sampling sites were:

Forest seedling nurseries where cypermethrin is used to protect newly planted seedlings against arthropod infestation.

Intermittent storage sites for timber where cypermethrin is used to protect newly felled timber against outbreaks of arthropods.

Storm water from detached houses and villa gardens because the usage of pesticide products containing cypermethrin may result in these compounds reaching the storm water system.

Landfills receiving painted and impregnated building material. Three large landfills in southern Sweden were included in the study and samples were taken in surface waters and sediments influenced by the landfills and in storm water within the landfill.

The sampling plan and the measured matrices is shown in table 2.4.

Table 2.4 Sampling matrices and the types of sources for Cypermethrin. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programme.

Sampling matrices Cypermethrin										
Sources	Soil	Sludge	Incoming water	Outgoing water	Surface water	Storm water	Sediments from storm water manhole	Landfill leachate	Ground-water	Sediment
Background	3 / 0				2 / 0					3 / 0
Diffuse sources					1 / 1					
Waste water treatment plants		0 / 1	2 / 1	4 / 3						
At a locations influenced by the following sources										
a. Waste water treatment plants					1 / 2					1 / 0
Detached house gardens	3 / 0									
b. Storm water from detached houses						7 / 0				
c. Forest seedling nurseries	1 / 0				2 / 0			2 / 0		2 / 0
d. Storage sites for timber	32 / 0									
e. Landfills					1 / 0			11 / 0		1 / 0
f. Paint industries		1 / 0	1 / 0			3 / 0	3 / 0		2 / 0	0 / 1
g. Harbours / boat storage sites									1 / 0	
h. Agriculture	2 / 0				2 / 0				2 / 0	2 / 0
i. Storage sites for treated wood	2 / 0					1 / 0	5 / 0		1 / 0	
Total	40 / 0	1 / 1	3 / 1	4 / 3	9 / 3	11 / 0	8 / 0	11 / 0	8 / 0	9 / 1
Grand total					<u>103 / 11</u>					

2.1.5 Kathon

The most important sampling sites were:

Paint industries were the substance is still used as a biocide. Two smaller paint industries and one very large was included. Samples were taken in soil, sludge from an on site treatment plant (the larger industry), incoming water to the treatment plant, storm water, ground water and sediments.

Waste water treatment plants that receives waste water from a number of possible sources where the substance is used, including household usage and industrial usage.

Pulp and paper industries where Kathon is used as a slemicide to prevent microbial growth on machine equipment.

Single house sewage plants where water from single houses is treated in sand filters before reaching surface waters.

The original sample plan included sites impacted by production of household products. No such production site where Kathon was used was found in Sweden. These were replaced by paint industries and pulp and paper industries.

Regional sampling of kathon focused almost exclusively on sewage treatment plants.

The sampling plan and the measured matrices are shown in table 2.5.

Table 2.5. Sampling matrices and the types of sources for kathon. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programme.

Sampling matrices Kathon										
Sources	Soil	Sludge	Incoming water	Outgoing water	Surface water	Storm water	Sediments from storm water manhole	Landfill leachate	Ground water	Sediment
Background	3 / 0									3 / 0
Diffuse sources					1 / 3	3 / 0				0 / 1
Waste water treatment plants		2 / 23	2 / 13	2 / 36						
At a locations influenced by the following sources										
a. Waste water treatment plants					2 / 4				1 / 0	2 / 1
b. Single house sewage plants		1 / 0		3 / 0					2 / 0	1 / 0
e. Landfills						0 / 1		0 / 1		1 / 0
f. Pulp and paper industries		3 / 0	4 / 0	3 / 0	1 / 0					3 / 0
f. Paint industries		1 / 1	1 / 0	1 / 1		1 / 0	3 / 0		2 / 0	2 / 0
h. Hospitals				0 / 2						
i. Storage sites for treated wood							2 / 0			1 / 0
j. Household						3 / 0			1 / 0	
Total	3 / 0	7 / 24	7 / 13	9 / 39	4 / 7	7 / 1	5 / 0	0 / 1	6 / 0	13 / 2
Grand total										<u>54 / 87</u>

2.1.6 Propiconazole

The most important sampling sites were:

Storage sites where painted and/or impregnated wood is stored outdoors. Samples were mostly taken in storm water and storm water sediments.

Landfills receiving painted and impregnated building material. Three large landfills in southern Sweden were included in the study and samples were taken in surface waters and sediments influenced by the landfills and in storm water within the landfill.

Paint industries where the substance is still used as a biocide. Two smaller paint industries and one very large was included. Samples were taken in soil, sludge from

an on-site treatment plant (the larger industry), incoming water to the treatment plant, storm water, ground water and sediments.

Originally, the sample plan included golf courses. These were however excluded since no golf courses where this substance is used could be found.

The sampling plan and the measured matrices is shown in table 2.6.

Table 2.6 Sampling matrices and the types of sources for propiconazole. The first value denotes samples taken within the national screening programme. The second value (after the slash) denotes samples financed by the regional screening programme.

Sampling matrices Propiconazole										
Sources	Soil	Sludge	Incoming water	Outgoing water	Surface water	Storm water	Sediments from storm water manhole	Landfill leachate	Ground-water	Sediments
Background	3 / 0				1 / 0					3 / 0
Diffuse sources					1 / 2					1 / 0
Waste water treatment plants		3 / 4	2 / 1	5 / 2						
At a locations influenced by the following sources										
a. Agriculture	2 / 0				2 / 0				2 / 0	2 / 0
b. Storage sites for treated wood	2 / 0				2 / 0	1 / 0	5 / 0		1 / 0	4 / 0
c. Forest seedling nurseries									1 / 0	
d. Landfills					1 / 0			11 / 2		1 / 0
e. Waste water treatment plants					1 / 1					1 / 0
gf. Paint industries		1 / 0	1 / 0			3 / 0	3 / 0		2 / 0	0 / 1
g. Harbours / boat storage sites									1 / 0	
h. Household						2 / 0				
Total	7 / 0	4 / 4	3 / 1	5 / 2	8 / 3	6 / 0	8 / 0	11 / 2	7 / 0	12 / 1
Grand total					<u>71 / 13</u>					

2.2 Sampling methods

Sampling instructions were given to all sampling personnel. The instructions explained sampling procedures and handling of samples during transport.

2.2.1 Soil

Soil was sampled from the topmost layer after the removal of dead and living plant parts. Also, stones and larger objects were avoided. Soil samples were collected into diffusion proof clean sampling plastic bags and sent to the laboratory within a day of sampling. Samples were kept cold until analysis.

2.2.2 Sediment

Sediment samples were collected by means of a core sampler. All sediment samples were transferred to pre burned and dark glass jars and sent to laboratory within one or two days of collection. They were stored cold until analysis.

2.2.3 Sewage Treatment Plant (STP) sludge and water

The staff at the sewage treatment plants collected the sludge samples and water samples in acid rinsed pre burned dark glass bottles. All STP samples were sent to the laboratory within one or two days of collection. They were stored cold until analysis.

2.2.4 Fish

Only perch (*Perca fluviatilis*) was used in this study. Samples from Abisakojaure and Krageholmssjön were supplied from the Environmental Specimen Bank at the Museum of Natural history (A. Bignert and colleagues). Fish from Ljusacknen and all other fish were collected using fishing net. All fish samples were stored frozen until analysis.

2.2.5 Water

Unfiltered water was collected in clean in acid rinsed pre-burned dark glass bottles. Water samples were cold until analysis.

2.3 Analytical methods

Analytical methods are given in table 2.7 below.

Table 2.7 Analytical methods for the substances investigated in the screening study.

Substance	Extraction	Cleanup	Internal standard	External standard	Instrument	Method
Tolyfluanide solid matrices	Hexane/ Cyclohexane/ Acetone	No	3	Tolyfluanide	GC-MS	Internal
Tolyfluanide water	Direct injection	No	3	3	LC-MS-MS	internal
Chlorothalonil	Dichloromethane, pH2 and pH 10	No	3	Chlorothalonil	GC-MS	Modified EN-12918
Diuron water	Direct injection	No	3	3	LC-MS-MS	internal
Diuron solid matrices	Acetonitrile		Fenuron and Prometryn in MeOH	Diuron	LC-DAD	Internal
Cypermethrin	Hexane/ Cyclohexane/ Acetone	No	no	Cypermethrin	GC-MS	Internal
Propiconazole	Dichloromethane, pH2 and pH 10	No	no	Propiconazole	GC-MS	Modified EN-12918
Kathon	Mixture of polar solvents	SPE in solid matrices	3	Kathon	GC-MS	Internal

3 Results and discussion

3.1 Tolyfluanid

Tolyfluanid was detected in the sediments of two storm water manholes at a paint industry (0,26 and 0,85 mg/kg) and in soil (0,3 mg/kg) at a storage site for treated wood. The limit of quantification in water was 0.01 – 10 µg/l and 0.01 – 0.1 mg/kg in soils and sediments.

Previous studies regarding the degradability and volatility in soils, sediment and surface waters indicate that tolyfluanid rapidly hydrolyses in the environment (<http://www.apvma.gov.au/publications/prstol.shtml>, EFSA 2005) which could be the major explanation for the low degree of detection in this study.

The main metabolite of tolyfluanid is dimethylaminosulfotoluidide which has a similar toxicity compared to tolyfluanid but a lower mobility. This substance has been found in soil extracts on a few occasions (Roberts and Hutson 1998).

Recently (2007) a previously unknown degradation product (dimethylsulfamide) of tolyfluanid has been discovered (http://www.kemi.se/SiteSeeker/HitCounter.aspx?url=http%3a%2f%2fwww.kemi.se%2fupload%2fBekampningsmedel%2fEuparen_aterkallande_av_godkannandet.pdf&pageid=4694.1&word=tolyfluanid). This degradation product can in turn form nitrosamines when drinking water is treated with ozone. Since nitrosamines are known carcinogenics and German authorities have found dimethylsulfamide in both surface water and groundwater, the usage of tolyfluanide in open field agriculture has been revoked in the European Union. The usage at forest seedling nurseries had consequently been discontinued for at least a year before the measurements in this study were done which may be one more reason why tolyfluanide was not detected.

However, tolyfluanide is still used in paint formulations. The substance was detected in two samples of sediments from storm water manholes at a paint industry where tolyfluanide is used daily. No tolyfluanide was detected in the storm water, groundwater, untreated waste water, sludge from waste water treatment or soil samples collected at paint industries. Soils below building facades that had been painted 1 – 2 years ago with paint that contained 0.2% of tolyfluanide did not contain any measurable concentrations of tolyfluanide.

Previous studies show that tolyfluanide leach from freshly painted surfaces at a rate of 0.4% / 100 days (Togerö 2004). This indicates that the leaching should have been ongoing. The lack of detection below painted surfaces may be because the rate of

leaching from the facade is slower than the rate of degradation in the soil, or that the concentrations in the soil do not become high enough for detection to be possible.

Tolyfluanide is regularly sampled within the regional monitoring of pesticides (table 3.1). The substance has never been detected within these sampling programs.

Table 3.1 Monitoring data for Chlorothalonil from regional and local monitoring of pesticides in surface waters, ground waters and drinking waters. The database is maintained by the Swedish Agricultural University with financing from the Swedish Environmental protection Agency. All data is supplied from regional monitoring of pesticides.
<http://vv.mv.slu.se/>.

Years		Number of analyses	Number of occasions when detected	Median concentration	Maximum concentration
Ground water (µg/l)	Before 1990 - 1997	265	0	0	0
	1998 - 2007	199	0	0	0
Surface water (µg/l)	Before 1990 - 1997	630	0	0	0
	1998 - 2007	86	0	0	0
Drinking water (µg/l)	Before 1990 - 1997	149	0	0	0
	1998 - 2007	52	0	0	0

Conclusions and recommendations

On the one hand, tolyfluanide was found on two occasions in connection to a major point source (a paint industry). On the other hand, tolyfluanide was not encountered in a large number of other matrices and is not detected within the ongoing monitoring performed by the Swedish Agricultural University. Consequently, there is no further need for screening or monitoring of tolyfluanide. The information on degradation products in German surface waters and ground waters needs to be reviewed to determine whether a limited screening of these degradation products are necessary or not.

3.2 Chlorothalonil

Chlorothalonil was not detected in any of the samples. The limit of quantification in water was 0.01 – 10 µg/l and 0.01 – 0.1 mg/kg in soils and sediments.

The usage of chlorothalonil within agriculture has been discontinued for a long time (end of the 1990s) due its carcinogenic effects. It is still used in paint and wood preservation products (most likely at very low concentrations). Despite this, no chlorothalonil was found at paint factories or where treated wood products are stored. The low concentrations used in paint and products for wood treatment may mean that the usage is “diluted” to such a degree that the substance is difficult to detect in the environment.

Another reason for the lack of detection may be that biodegradation is expected to be an important fate process both in water and soils (HSDB). Chlorothalonil biodegrades mainly through dechlorination yielding isophthalonitrile degradation products and there are indications that these may be more stable in the environment than the mother compound (HSDB). Hydrolysis only occurs at pH > 7 and it is uncertain how important this process is for the environmental fate of chlorothalonil.

Chlorothalonil is expected to have low mobility in soils based on Koc values in the range of 1800 to 2400 (Table 1.2). Consequently, the transport to surface waters and/or ground waters should be very limited.

Apart from the low usage, this may also explain why chlorothalonil has not been found within the Swedish regional aquatic monitoring of pesticides (table 3.2)

Table 3.2 Monitoring data for Chlorothalonil from regional and local monitoring of pesticides in surface waters, ground waters and drinking waters. The database is maintained by the Swedish Agricultural University with financing from the Swedish Environmental protection Agency. All data is supplied from regional monitoring of pesticides.
<http://vv.mv.slu.se/>.

	Years	Number of analyses	Number of occasions when detected	Median concentration	Maximum concentration
Ground water (µg/l)	Before 1990 - 1997	194	0	0	0
	1998 - 2007	38	0	0	0
Surface water (µg/l)	Before 1990 - 1997	616	0	0	0
	1998 - 2007	8	0	0	0
Drinking water (µg/l)	Before 1990 - 1997	116	0	0	0
	1998 - 2007	19	0	0	0

Conclusions and recommendations

There is no further need for screening or monitoring of chlorothalonil. There is no information in the literature that the degradation products may constitute serious environmental problems which in combination with the low (and decreasing usage – figure 1.2) suggests that the metabolites are not of any concern for future screening either.

3.3 Diuron

Diuron was detected in 15 samples from paint industries, landfills, a storage site for treated wood and waste water treatment plants. Diuron was also found in sediment and water from reference lakes. The results are presented in table 3.3 below. The limit of quantification in water was 0.02 – 0.04 µg/l and 0.01 – 0.05 mg/kg in soils and sediments.

Table 3.3 Samples where diuron has been detected

Source	Matrix	Number of samples	Result
Paint industry	Storm water	2	0.05 - 0.21 µg/l
Paint industry	Groundwater	2	0.06 - 0.4 µg/l
Paint industry, waste water treatment plant	Incoming water	1	32 µg/l
Paint industry, waste water treatment plant	Sludge	1	284 mg/kg DM
Landfill	Leachate	3	0.05 - 0.09 µg/l
Background lake (abiskojaure)	Surface water	1	0.02 µg/l
Background lake (Krageholmssjön)	Sediment	1	0.086 mg/kg DM
Background area (Krageholmssjön)	Soil	1	0.015 mg/kg DM
Waste water treatment plant	Sludge	1	0.063 mg/kg DM
Waste water treatment plant	Surface water	1	0.02 µg/l
Storage for treated wood	Storm water sediment	1	0.0188 mg/kg DM

Diuron was detected in three samples from two of the background locations; in the water of Abiskojaure, in sediments of Krageholmssjön and in soil from the area around Krageholmssjön. Krageholmssjön is situated in a agricultural area and the findings may be because of earlier agricultural use, especially considering that no railway embankments or major roads are in the vicinity of the lake. It is probably not easy to find background lakes that are not exposed to any agricultural chemicals in the agricultural areas of southern Sweden, and it is not a major surprise to find diuron in Krageholmssjön.

The findings of diuron in lake water of Abiskojaure are more surprising given that this lake is situated in a very unpopulated area of Northern Sweden. Two explanations are possible. Firstly, there is a major railway within 4 km of the lake and the Diuron found may reflect earlier use at the railway embankments. The other possible explanation is national or global atmospheric transport of diuron through the atmosphere to northern regions. Earlier studies in France (Scheyera et al. 2007) showed that nearly all rain water samples contained diuron. This demonstrates that diuron is probably a common substance in atmospheric deposition.

The usage of diuron on railway embankments and roads sides has been discontinued for a long time since diuron was banned in plant protection products due to its classification as a carcinogenic compound. It is however still widely used in USA. One reason for its popularity as a weed killer is its long residual activity, a quality that has also led to it being a groundwater contaminant of concern (Cederlund m.fl.

2007). A compilation of data from investigations at railway embankments or railway station areas by the Swedish Railway Administration showed that diuron was found at approximately 1/3 of the sampled locations. It should be noted that several of these investigations were focused on delineating the extent of known diuron pollution which indicates that the rate of occurrence was severely overestimated. The number of samples close to railway embankments in the present study may have been too low to “find” diuron at these types of locations.

However, since the occurrence at railway embankments is a known phenomenon this screening focused more on other sources related to the fact that diuron has been used in paint and wood protection products.

Diuron was detected both in the incoming waste water and in sludge from the waste water treatment plant at the paint industry. The effluent was not sampled. Three storm water manholes at the site were sampled for water and sediments. Diuron was detected in two of these water samples but not in any of the sediment samples. Diuron was also detected in two groundwater samples from the paint industry. It is interesting that other biocides investigated within this screening study (propiconazole and tolylfluanide) with a much higher usage in the paint factory were not detected to the same degree at the site. The explanation is probably a much higher persistence of Diuron compared to tolylfluanide and propiconazole.

Diuron was detected in surface waters downstream a waste water treatment plant, but not in the upstream sample. It was also detected in sludge from another waste water treatment plant. Diuron was previously measured in sludge from 6 different waste water treatment plants in Sweden (Kylín 2005) but was not found in any of them. The stream where diuron was found mainly flows through agricultural areas, and diuron has been found in these types of streams before (table 3.4). However, since no diuron was found upstream of the waste water treatment plant it is possible that the plant was the source.

Finally, diuron was detected in three samples from two landfill sites that both received painted and treated wood which is the most likely source of diuron in the landfill leachates.

Diuron is a persistent herbicide with a low degree of biodegradability (HSDB, Cederlund et al 2007) which is probably the most important reason for its reoccurring detection in a number of matrices. However, most of the occurrences were in the vicinity of a major point source (a paint factory) and in many cases it was not detected at all. The proposed environmental quality standard of Diuron according to the water framework directive is 0.2 µg/l. In relevant environmental matrices (which exclude incoming water and solid matrices) this level was exceeded in one groundwater sample and in one storm water sample. Dilution processes will

probably ensure that the EQS value is not exceeded in any surface water that is connected to the storm water and ground water.

Diuron is regularly sampled within regional monitoring of pesticides (table 3.4). Diuron has been found in 0.2-1% of the cases and the occurrence has not diminished when comparing the periods 1990 – 1997 and 1998 - 2008 despite the fact that its use as a weed killer was discontinued in the early 1990s.

Table 3.4 Monitoring data for Diuron from regional and local monitoring of pesticides in surface waters, ground waters and drinking waters. The database is maintained by the Swedish Agricultural University with financing from the Swedish Environmental protection Agency. All data is supplied from regional monitoring of pesticides. <http://vv.mv.slu.se/>.

	Years	Number of analyses	Number of occasions when detected	Median concentration	Maximum concentration
Ground water (µg/l)	Before 1990 - 1997	221	2	1.03	2.0
	1998 - 2007	3714	16	0.0855	0.2
Surface water (µg/l)	Before 1990 - 1997	518	0	0	0
	1998 - 2007	1064	11	0.0485	0.2
Drinking water (µg/l)	Before 1990 - 1997	125	0	0	0
	1998 - 2007	2530	5	0.1	0.16

Conclusions and recommendations

Diuron is intermittently measured by other national and regional authorities at those types of locations where the substance may occur (especially railway embankments) and yearly in streams, surface waters and groundwater. Consequently, there is no need for further screening of diuron in abiotic matrices. However, it may be pertinent to redesign the regional monitoring of pesticides to include non-agricultural sites since diuron should be viewed as an industrial/product biocide more than an agricultural biocide. Given the indications that Diuron is spreading to more remote areas, a limited screening study of diuron in biotic matrices may be warranted. Such a study could use material from the environmental specimen bank at the department of contaminant research, Swedish museum of natural history to study both the levels in biota at present and in older samples to ascertain if the concentrations are declining or not. Finally, diuron levels in atmospheric deposition and in air may need to be screened to evaluate the atmosphere as an important source of this substance to Swedish surface waters. .

3.4 Cypermethrin

Cypermethrin was detected in four samples:

Topsoil (0 – 10 cm) in proximity to storage sites for timber: 0.15 and 0.39 mg/kg

Storm water from detached houses: 0.1 and 0.45 µg/l

The limit of quantification in water was 0.01 – 1 µg/l and 0.02 – 0.1 mg/kg in soils and sediments.

The concentrations found in the soils in this study are equal to or somewhat lower than the Dutch maximum permissible concentration (MPC) of 0.39 mg/kg (table 1.4) which indicates that they may cause negative effects on soil biota. The frequency of occurrence was quite low (two of 34 soils samples). On the other hand, cypermethrin was (as far as known) applied to these sites approximately 6- 8 months before the sampling. Since cypermethrin degrades rapidly in soil under aerobic conditions with measured half lives of 4 days to 12 weeks (HSDB) it may be that the concentrations were higher at more locations closer to the time of application.

A number of different biodegradation products of cypermethrin are known [for example: 3-(4-hydroxyphenoxy)benzyl ester; 3-(4-hydroxyphenoxy)benzoic acid; 3-phenoxybenzoic acid; and (+ or -)-cis- and (+ or -)-trans-3-(2-dichlorovinyl)-2,2-dimethyl-cyclopropanecarboxylic acid] (HSDB). The environmental fate and (eco)toxicity of the degradation products is not well known, but given the results they might merit further studies.

Deeper soil (10 – 20 cm below surface), below where cypermethrin was found did, not contain cypermethrin above the quantification limit. This indicates that leaching had not taken place since application of cypermethrin to the timber. In accordance, cypermethrin is expected to have no or very low mobility based upon a range of Koc values from 5,800 to 160,000 (table 1.4).

This may also explain why previous studies in Sweden of cypermethrin in streams in the vicinity of storage sites for timber only showed trace concentration in the sediments (Goedkoop and Kreuger 2006). It may be that cypermethrin that is not applied in very close vicinity to surface waters is mainly a soil problem because of a limited leaching to surface waters.

This may also explain why cypermethrin has not been found within the regional monitoring of pesticides that is done by the Swedish Agricultural University and financed by the Swedish Environmental protection Agency (table 3.5).

Table 3.5 Monitoring data for Cypermethrin from regional and local monitoring of pesticides in surface waters, ground waters and drinking waters. The database is maintained by the Swedish Agricultural University with financing from the Swedish Environmental protection Agency. All data is supplied from regional monitoring of pesticides. <http://vv.mv.slu.se/>.

	Years	Number of analyses	Number of occasions when detected	Median concentration	Maximum concentration
Ground water (µg/l)	Before 1990 - 1997	761	0	0	0
	1998 - 2007	350	0	0	0
Surface water (µg/l)	Before 1990 - 1997	1037	0	0	0
	1998 - 2007	255	0	0	0
Drinking water (µg/l)	Before 1990 - 1997	361	0	0	0
	1998 - 2007	125	0	0	0

Storm water was sampled from five separate areas with detached houses and villa gardens. Cypermethrin was found in storm water from two of these areas at concentrations 4500 higher than the guideline value for Swedish surface waters (0.0001 - 0.0002 µg/l, table 1.4). The storm water will be heavily diluted in surface waters or treated in sewage treatment plants and the levels found do not give rise to any immediate concern. Nevertheless, the results demonstrate that household usage of insecticide products may be a more important source of cypermethrin (and perhaps other pesticides) than previously known.

Conclusions and recommendations

The results may merit further screening of cypermethrin in soils surrounding storage sites for timber at times closer to when the insecticide is applied. This is only of interest if the use of cypermethrin for protection of felled timber continues. This practice has to be approved by local authorities and it is not certain that such approval will always be forthcoming.

Given that two out of five storm waters from areas with detached houses contained cypermethrin, future screening of cypermethrin (and other pesticides used in villa gardens) may be merited.

Since cypermethrin degrades easily giving rise to a number of degradation products it could also be of interest to focus on these metabolites rather than the parent compound.

3.5 Kathon

Kathon was not detected in any of the samples. The limit of quantification in water was 1 – 100 µg/l and 0.05 – 0.1 mg/kg in soils and sediments.

Kathon is a widely used biocide in a number of both household products (Fewings and Menné 1999,) and industrial applications, and it was somewhat unexpected that it was never found in incoming water to sewage treatment plants. It was neither found in incoming, water, outgoing water or sludge at paper mills where it is used to combat microbial growth on machine equipment.

Literature data indicate that the most likely reason for lack of detection is that the isothiazolinones MI and CMI (see table 1.5 for explanation of MI and CMI) are easily (bio)degraded (Madsen et al. 2001, Rafoth et al.2007)

90% of of MI and 70% of CMI was transformed in 24 hours in an aerobic experimental river sediment-water giving a calculated half life of only 9 hours and 17 hours for MI and CMI respectively (Madsen et al. 2001). Both compounds were transformed to several unidentified polar metabolites. At the end of the experiments metabolites that were bound in the sediment corresponded to 55% - 57% of the added mother compound which indicates that the metabolites are more stable than the original compound.

The biodegradability of CMI has also been examined under anoxic conditions in a river sediment-water system giving a half life of 4.6 h. It has been proposed that the anaerobic degradation of CMI leads to the same type of metabolites as proposed for aerobic degradation of MI and CMI.

The ultimate aerobic biodegradability (i.e. complete degradation to carbon dioxide) of MI and CMI has been examined in an OECD test (301B). The ultimate biodegradability of CMI and MI were close to the pass level for ready biodegradability (Madsen et al. 2001).

CMI and CI also degrades quickly in natural river waters. The compounds disappeared completely after 4 – 8 days in river Rhine water kept at 23°C and by approximately 60 – 90% after 21 days in river Rhine water stored at 4 °C (Rafoth et al 2007).

The Kathon compound MI and CMI were measured together with three other isothiazolinone compounds in incoming and outgoing water from a very large municipal wastewater treatment plant in Germany. CMI and MI were detected in one of seven incoming water samples at a level of 0.5 µg/l. which is below the quantification limit in this study (Rafoth et al. 2007). In the same samples another isothiazolinone compound (1,2-benzo isothiazolinones; BIT) was frequently found at concentrations ranging from 1.5 – 3 µg/l. BIT is increasingly replacing CMI in cleaning agents, paints, adhesives etc (Rafoth et al. 2007) although the usage in shampoos and liquid soaps is still dominated by CMI (Rafoth et al. 2007).

Neither CMI, MI or any other isothiazolinone compounds were found in effluent waters from the municipal wastewater treatment plant or in major German rivers such as Rhine, Main, Neckar or Danube, or in small German rivers with relatively large contributions from wastewater treatment plants (Rafoth et al. 2007). These results were interpreted such that the isothiazolinones were completely eliminated before reaching wastewater treatment plants and in the plants themselves.

Conclusions and recommendations

Based on the results from this screening, the German screening study and experimental studies on biodegradation there is no need for further screening of the Kathon compounds CMI or MI or any other isothiazolinone compounds. However, the need for further screening of isothiazolinone biodegradation products can not be excluded since the stability and ecotoxicity of the degradation products in the environment is largely unknown.

Some Kathon compounds are also used as biocides in boat paints. Since these specific Kathon compounds were not investigated in this screening study, harbor sediment was not included in the sampling plan for Kathon CMI and CI. This may be something to consider for future screening studies that could also focus on other boat paint biocides.

3.6 Propiconazole

Propiconazole was the most commonly detected substance in this study since it was found in 21 of 71 samples from a paint industry, landfills, and storage sites for treated wood. The results are presented in table 3.6 below. The limit of quantification in water was 0.03 – 4 µg/l and 0.03 – 0.1 mg/kg in soils and sediments.

Table 3.6 Samples where propiconazole has been detected

Source	Matrix	Number of samples	Result
Paint industry	Storm water	3	0.67 - 85 µg/l
Paint industry	Groundwater	2	0.28 - 7.9 µg/l
Paint industry	Storm water manhole sediments	3	0.22 - 2.5 mg/kg DM
Paint industry, waste water treatment plant	Incoming water	1	150 µg/l
Paint industry, waste water treatment plant	Sludge	1	23 mg/kg DM
Storage for treated wood	Storm water manhole sediments	5	0.12 - 0.48 mg/kg DM
Storage for treated wood	Storm water	1	2.1 µg/l
Storage for treated	Soil	1	0.32 mg/kg DM

wood			
Landfill	Leachate	4	0.15 - 0.8 µg/l

Propiconazole has previously been found in Swedish surface waters (table 3.7) but not in sediments in agricultural areas (Adielson et al. 2005). In a previous screening study in Sweden, propiconazole was found in 2 out of 24 sludge samples from waste water treatment plants and in 2 out of 14 effluent water samples. Furthermore, propiconazole was also found in 1 out of 6 leachate samples from landfills and in a storm water sample and storm water sediments in the vicinity of a wood impregnation factory (Remberger et al. 2005).

In this study, focus was on storage sites where painted and/or impregnated wood is stored outdoors, landfills receiving painted and impregnated building material and paint industries where the substance is still used as a biocide in paint formulation. Propiconazole was detected in all samples that were taken at paint industries, including storm water and groundwater samples.

The concentrations can be compared to the guideline value for surface waters derived by the Swedish Chemicals Agency (Naturvårdsverket 1998). The guideline value of 7 µg/l represents the highest concentration where no negative ecological effects are expected. This value is exceeded in one storm water sample (85 µg/l) and one ground water sample (7.9 µg/l).

Propiconazole was also detected in all but one of the samples from storage sites for treated wood. Concentrations from these sites are generally lower than the samples from paint industries. The substance was also detected in four of nine landfill leachate samples. Concentrations are well under the surface water guideline value mentioned above and the most probable source of propiconazole in the landfill leachate is treated and painted wood products that are deposited at the landfill.

This study confirms that propiconazole may be a common contaminant in the vicinity of sites where paint is produced, painted products are stored and where painted products are deposited. This is despite a possibly high degree of biodegradability. The estimated half-life of propiconazole in aerobic soils is about 40-70 days and in aerobic waters is about 25-85 days (HSDB).

Propiconazole is regularly sampled within the regional monitoring of pesticides (Table 3.7). It is found in surface waters in these studies, and the occurrence seem to increase from 1990 - 1997 (detected in 0.3% of sampled waters) to the period 1998 – 2007 (detected in 4% of sampled waters).

Table 3.7 Monitoring data for Propiconazole from regional and local monitoring of pesticides in surface waters, ground waters and drinking waters. The database is maintained by the Swedish Agricultural University with financing from the Swedish Environmental protection Agency. All data is supplied from regional monitoring of pesticides.

<http://vv.mv.slu.se/>.

	Years	Number of analyses	Number of occasions when detected	Median concentration	Maximum concentration
Ground water (µg/l)	Before 1990 - 1997	765	0	0	0
	1998 - 2007	388	0	0	0
Surface water (µg/l)	Before 1990 - 1997	996	3	0.5	0.5
	1998 - 2007	410	16	0.03	1
Drinking water (µg/l)	Before 1990 - 1997	362	0	0	0
	1998 - 2007	135	0	0	0

Conclusions and recommendations

This and earlier screening studies show that propiconazole can be found in the vicinity of sites where water based paints are produced or where treated wood products are stored. However, the substance is not found at background lakes and only seldom within the regional monitoring program of pesticides (Table 3.7). Also, when detected in surface waters the levels are well below the national guideline value (Table 3.7). The substance is not classified as being bioaccumulative.

As long as no new information surfaces on the bioaccumulative potential or the (eco)toxicity of propikonazole no further screening is warranted.

However, the increasing levels seen in the regional monitoring (Table 3.7) together with the results from this study merits that the levels of propikonazole is continuously monitored and evaluated. As is the case for diuron, it may be pertinent to redesign the regional monitoring of pesticides to include non-agricultural sites, since propikonazole should be viewed as an industrial/product biocide as well as an agricultural biocide.

4 Conclusions and recommendations

In general, biocides do not seem to constitute a major problem in the Swedish environment. Even if some of them occur frequently close to important emission sources, the levels are usually well below risk levels. This is also supported by the results from an earlier screening study of biocides (Remberger et al. 2005). The reason for these results is probably a combination of low amounts used in relation to the size of the environmental compartments they are emitted to, and a generally high degree of (bio)degradability.

The recommendations for the specific substances are:

Tolyfluanide

There is no further need for screening or monitoring of tolyfluanide. It may be relevant to review German screening studies on the occurrence of degradation products of tolyfluanide before deciding if these should be investigated in the future.

Chlorothalonil

There is no further need for screening or monitoring of chlorothalonil based on the low amounts used and the lack of detection in this study.

Diuron

There is no need for further screening studies of diuron in abiotic matrices based on the fact that the substance is regularly measured within the regional monitoring program and by other authorities. A limited screening in biotic matrices may be warranted. There may also be a need for a limited screening of Diuron levels in air to evaluate the atmosphere as an important source of this substance.

Cypermethrin

If the use of cypermethrin for protection of felled timber continues it may be warranted with measurement in the soil close to the time of application to elucidate the possible effects on soil biota. Since two out of five storm waters from areas with detached houses contained cypermethrin future screening of cypermethrin (and other pesticides used in villa gardens) may be merited. Since cypermethrin degrades easily giving rise to a number of degradation products it could also be of interest to focus on these metabolites rather than the parent compound.

Kathon

Based on the low degree of occurrence in this study and a German screening study and the proven low persistence of these types of compounds there is no need for

further screening of the Kathon compounds CMI or MI or any other isothiazolinones. However, the need for further screening of isothiazolinone biodegradation products can not be excluded since the stability and ecotoxicity of these compounds in the environment is largely unknown. Some Kathon compounds (isothiazolinones) are also used as biocides in boat paints. These were not investigated in the present study, and this may be the focus of future screening studies since boat paints are in direct contact with the surface water environment. On the other hand, the high biodegradability of kathon compounds, may eliminate the need for such studies.

Propiconazole

The results from this screening and a previous screening of propiconazole shows that the compound mostly occurs in the vicinity of sites where paint is produced or where treated wood products are stored. Since the compound is regularly monitored there is no need for further focused screenings of this compound. However, the increasing levels seen in the regional monitoring (Table 3.7) together with the results from this study merits that the levels of propikonazole is continuously monitored and evaluated.

Regional monitoring of pesticides

The regional aquatic monitoring of pesticides includes a number of substances that should be viewed as industrial/product biocides as well as agricultural biocides. The results from this (diuron and propiconazole) and other screening studies of such biocides may motivate a redesign of the yearly monitoring of pesticides. This could mean a transition to include sites impacted by industrial and urban activities as well as waste water treatment plants and landfills.

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