REPORT

Results from the Swedish Screening Programme 2006

Subreport 3: Zinc pyrithione and Irgarol 1051

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Title and subtitle of the report

Results from the Swedish National Screening Programme 2006.

Subreport 3: Zinc pyrithione and Irgarol 1051

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of zinc pyrithione. Also the concentrations of irgarol 1051, zinc (Zn) and lead (Pb) were measured in the study.

Keyword

Zinc pyrithione, irgarol 1051, Screening

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Sammanfattning

IVL har på uppdrag av Naturvårdsverket genomfört en screening av zinkpyrition, samt irgarol 1051. Två metaller (Zn, Pb) inkluderades även i analyserna.

Zinkpyrition och irgarol 1051 är biocider som bl a används i båtbottenfärg. Zinkpyrition används också i vissa kosmetiska produkter, t ex mjällschampo. Då ämnenas användningsområden i samhället är breda, kan man antaga att spridningen sker via flera olika källor, t ex punktkällor och hushåll. Emissioner kan även förväntas i anslutning till hamnar, varv, båtklubbar och marinor.

Det huvudsakliga syftet med föreliggande studie var att få en uppfattning om koncentrationer i olika matriser i miljön, att belysa tänkbara transportvägar samt bedöma huruvida uppmätta koncentrationer kan tänkas ha någon miljöpåverkan. Även eventuellt upptag i biota och människa undersöktes.

Screeningprogrammet innefattade mätningar i bakgrundsområden och i närheten av möjliga punktkällor. Mätningar gjordes också i urbana områden vilket avspeglar diffusa emissioner från samhället. Provtyperna var vatten (in- och utgående avloppsvatten, ytvatten, lakvatten samt processvatten ifrån relevant industri), sediment, slam, biota (fisk) och human urin. Totalt insamlades 124 prover varav 112 analyserats m a p zinkpyrition, 115 analyserats m a p zink och bly, och 118 analyserats m a p irgarol 1051.

Zinkpyrition detekterades endast i tre vattenprover (ingående vatten till avloppsreningsverk samt utgående processvatten ifrån en industri) i koncentrationerna 1.9, 17 and 32 µg/l. I alla övriga prover kunde zinkpyrition ej påvisas över detektionsgränsen. Det var således ej möjligt att korrelera förekomst av zinkpyrition med halten zink.

Irgarol 1051 kunde påvisas i 40 % av alla vattenprover (0,006-0,014 µg/l), 50 % av alla slamprover (2,1-54 µg/kg dw) och i 70 % av alla sedimentprover (2,5 – 20 µg/kg dw). Varken zinkpyrition eller irgarol 1051 kunde detekteras i urin.

Sammanfattningsvis så kunde zinkpyrition endast detekteras i tre prover och zinkpyrition kan därför inte anses vara ett miljömässigt problematisk ämne. Fortsatt monitorering av zinkpyrition rekommenderas därför inte.

- Det var ej möjligt att korrelera påvisade halter av zinkpyrition till detekterade halter av zink.
- Den mycket låga detektionsfrekvensen av zinkpyrition, den stora användningen tilltrots, indikerar att zinkpyrition bryts ner mycket fort i miljön.
- Irgarol 1051 detekterades i ca 70 % av alla sedimentprover (i alla sedimentprover utom bakgrundsproverna). Detta är ej överraskande då ämnet främst används som biocid i båtbottenfärg. Irgarol 1051 detekterades dessutom i nästan 50 % av alla slamprover vilket föranleder följande slutsatser; 1) ämnet används överallt i Sverige (inte bara vid kusten), samt 2) det finns möjligen andra källor och användningsområden för irgarol 1051 än de hittills rapporterade då det så ofta återfinns i slam.
- Irgarol 1051 detekterades oftare i utgående vatten ifrån avloppsreningsverk än i ingående vatten. Anledningen till detta är okänd.

- Sediment och slam förefaller vara mycket lämpliga matriser för att studera spridning av irgarol 1051.
- Varken irgarol 1051 eller zinkpyrition kunde detekteras i humanurin.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006 performed a "Screening Study" of zinc pyrithione and irgarol 1051. These substances are biocides used as anti-fouling agents in products such as paints, anti-dandruff products and some medical products. Because of their common appearance in consumer products, zinc pyrithione and irgarol 1051 are likely to be emitted and distributed in the environment via a variety of sources, e.g. point sources and via consumer use. Emissions in areas with boating activities are also likely to occur.

The overall objectives of the screening were to determine the concentrations of the substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of uptake in biota and humans.

The screening programme included measurements in background areas and in the vicinity of potential point sources and/or "affected areas". Measurements were also carried out in urban areas reflecting diffuse emission pathways from the society. Sample types were water (surface water, in- and outgoing sewage water, industrial effluents, drinking water and landfill leachate) sediment, sludge, biota (fish) and human urine. A total of **124** samples were included. 112 samples have been analysed with respect to zinc pyrithione, 115 samples have been analysed with respect to zinc and lead, and 118 samples have been analysed with respect to irgarol 1051.

Zinc pyrithione (ZPT) was only detected in three water samples (representing ingoing water to STPs and one industrial effluent) in concentrations of 1.9, 17 and 32 µg/l. All other samples showed ZPT levels below the detection limit. It was not possible to identify any correlation with zinc levels. Irgarol 1051 occurred to a larger extent; it was detected in 40 % of water samples (0.006-0.014 µg/l), 50 % of sludge samples (2.1-54 µg/kg dw) and in 70 % of sediment samples (2.5 – 20 µg/kg dw). Neither zinc pyrithione nor irgarol 1051 was detected in human urine.

Conclusively, zinc pyrithione was only detected in three environmental samples, thus it is not regarded as problematic substance; no further monitoring is necessary.

- It was not possible to identify any correlation between zinc and zinc pyrithione.
- The limited detection frequency despite extensive use indicate high degradation rate of zinc pyrithione
- Irgarol 1051 was detected in approximately 70 % of all sediment samples (from all sampling sites apart from the background sites). This is not surprising considering the use of the substance as an antifouling component in boat paints. However irgarol 1051 was also detected in approximately 50 % of the sludge samples, suggesting; 1) a wide use of the substance throughout Sweden, and 2) other sources and usage applications of the substance than previously reported.
- Irgarol 1051 was more frequently occurring in STP effluent water, than in ingoing water. The reason for this is unclear.
- Sludge and sediment seem to be appropriate matrices to analyse with regard to irgarol 1051.
- Neither irgarol 1051 nor zinc pyrithione occurred in humane urine

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1 Introduction

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006 performed a "Screening Study" of phthalates, 1,5,9-cyclododecatriene, zinc pyrithione, pharmaceuticals and chromium(VI). These substances are emitted and distributed in the environment via a variety of sources, e.g. point sources and via use in consumer products. Pharmaceuticals in particular are frequently spread by domestic use.

The overall objectives of the screening were to determine the concentrations of the selected substances in a variety of media in the Swedish environment, 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 (phthalates, 1,5,9-cyclododecatriene and chromium) and uptake in biota.

The results are reported in five sub-reports according to Table 1.

Table 1. Substances / substance groups included in the screening

Substance / Substance group	Sub-report #.
Phthalates: Di-isononyl phthalate (DINP) Di-isodecyl phthalate (DIDP)	1
1,5,9-Cyclododecatriene (CDDT)	2
Zinc pyrithione	3
Pharmaceuticals: Fentanyl, Propofol, Dextropropxyphene, Bromocriptine, Thioridazine, Clozapine, Risperidone, Zolpidem, Sertraline, Fluoxetine, Flunitrazepam, Diazepam, Oxazepam	4
Hexavalent chromium (Cr(VI))	5

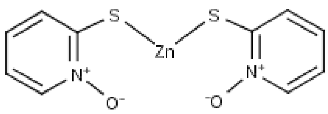
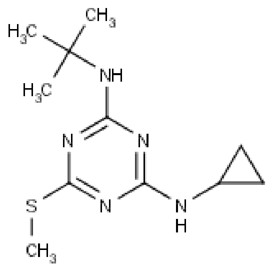
This sub-report considers the screening of zinc pyrithione (abbreviated ZPT and also known as pyrithione zinc). The samples selected for this screening investigation were also analysed for irgarol 1051, as it has a similar usage pattern. Two metals were also included; Zinc (Zn) with the aim of investigating possible co- or anti co-variation with ZPT levels. As a pure bonus substance, Lead (Pb) was included.

2 Chemical properties and toxicity

The chemical name of zinc pyrithione is zinc bis(pyridine-N-oxide-2-thiolate), or also bis(1-hydroxy-2(1H)-pyridinethiolato-O,S) zincate. It has the empirical formula $C_{10}H_8N_2O_2S_2Zn$. The substance features two pyridine-derived chelating ligands bound to zinc via their oxygen and sulphur atoms, respectively (see Table 2).

Irgarol 1051 or 2-methylthio-4-tert-.-butylamino-6-cyclopropylamino-s-triazine, which was included as an additional substance in the current screening, is used for similar purposes as of zinc pyrithione (ZPT). Its empirical formula is $C_{11}H_{19}N_5S$ and the molecular structure is shown in Table 2.

Table 2. Molecular structures and CAS-numbers of the selected screening substances of this report

Name	Use	Molecular Structure	CAS #	Synonyms
Zinc pyrithione	Anti-fouling, cosmetics		13463-41-7	ZPT, ZnP? Omadine Zinc, Zinc pyridine-2-thiol-1-oxide
Irgarol 1051	Anti-fouling		28159-98-0	N'-tert-Butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine

The Zn ion, where the pyrithione ligands bind, can be exchanged to other metal ions, which may lead to other metal complexes with two or three pyrithione ligands (MePT2/3), or to single pyrithione complexes such as sodium pyrithione and the $CuPT^+$-komplex (Sun et al., 1964). The speciation of complexes is determined by constants for each complex (see Table 3), as well as the concentration of pyrithione and the metals. In the marine environment, the presence of other ligands, both organic and inorganic, will influence the distribution of complexes. The constants are only determined for some of the complexes, but the order of complex strength is thought to be: Na<Fe<Mn<Zn<Cu.

Table 3. Physico-chemical properties of the selected compounds.

Name	Molecular Weight [g/mol]	Water Solubility [mg/l]	Melting point [°C]	Log Kow	Log Koc	Vapor pressure [Pa]	Stability const, log K1	Stability const, log K2
Zinc pyrithione	317.68	6	262	0.97	0.7	N/A	5.9	5.4
Irgarol 1051	253.37	6	133	2.8	2.38	1.5×10^{-5}	-	-

Due to the biocide action of metal pyrithiones, these substances are highly toxic to a number of pelagic species, especially algae. Its toxic effect most likely relies on the ability of an un-ionized pyrithione molecule to disrupt membrane transport by blocking the proton pump that energizes the transport mechanism (Chandler and Segel, 1978). In an illustrative calculation performed by the

Swedish Society for Nature Conservation (Sv; Naturskyddsföreningen, SNF), "half a tea spoon (3 ml) of a commercial anti-dandruff shampoo (containing 0.8 % w/w of zinc pyrithione) kills half the fish population in a 1 m^3 aquarium within 4 days time". In this example the fish is inserted into the aquarium at day 2 when approximately 90 % of the dosed zinc pyrithione is degraded, according to the kinetics of degradation (SNF, 2004). In the scientific literature, zinc pyrithione has been reported to be highly toxic to aquatic organisms (Table 4).

Table 4. A brief selection of ecotoxicological data on zinc pyrithione.

Test organism	Toxic Effect	Duration	Value [mg/l]	Reference
Suspension-cultured fish cell CHSE-sp	EC50	24 hours	0.18	Okamura et al., 2002
Juvenile rainbow trout (*Oncorhynchus mykiss*)	LC50	28 days	0.0046	Okamura et al., 2002
Zebra Fish (*Brachy-danio rerio*)	EC50	7 days	0.009	Goka, 1999
Japanese Medaka (*Oryzias latipes*)	EC50	7 days	0.005	Goka, 1999
Fish (*Cyprinodon variegates*)	LC50	96 hours	0.4	Madsen et al., 1999
Freshwater microalga (*Selenastrum capri-cornutum*)	EC50	3 days	0.015	Okamura et al., 2002
Macroalga (*Ceramium tenuicorne*)	EC50	7 days	0.0033-0.0064	Karlsson and Eklund, 2004
Crustacean (*Nitocra spinipes*)	LC50	96 hours	0.178-0.343	Karlsson and Eklund, 2004
Crustacean (*Mysi-dopsis bahia*)	LC50	96 hours	0.0063	Madsen et al., 1999
Oyster (*Crassostrea virginica*)	LC50	96 hours	0.0016	Madsen et al., 1999

In an extended report on the fate and toxicity of metal pyrithiones by TemaNord, it was concluded that for pelagic waters (open sea) a species sensitivity distribution (based on NOECs/LOECs from three trophic levels) indicates that a concentration of 0.2 nM (0.07 μg/l) of zinc pyrithione corresponds to a PAF (potentially affected fraction) of 5 %. Thus, at this concentration 95 % of the marine species are not affected (Dahlöf et al., 2005).

Irgarol 1051, is also a biocide used to prevent bio-fouling of submerged surfaces and it can replace tri-n-butyltin (TBT) as an active ingredient in *e.g.* antifouling paint used on ship´s hull, oil rig supports and buoys. Toxicological studies show that irgarol 1051 is highly toxic to many marine algae and sufficiently persistent to reach toxic levels in areas of high yachting activity, particularly in marinas with high activity (Agüera et al., 2000; Konstantinou and Albanis 2004).

Irgarol 1051 was the first biocide regarded as an environmental contaminant. It is indeed the most frequently detected anti-fouling agent worldwide and therefore used as a reference compound to Zn-pyrithione in this investigation. The first detection of irgarol 1051 in the environment was reported in 1993 in surface water in a marina in France. Since then, the occurrence of the biocide has been reported in a number of European countries and globally. Irgarol 1051 has also been reported to occur in the Scandinavian marine environment, e.g. at the Swedish West Coast, Stockholm Archipelago and Danish marinas. For more details, see the review by Konstantinou and Albanis (2004).

3 Environmental fate

The pyrithione complexes are neutral and hydrophobic, with a low solubility in water, resulting in a high affinity to organic matter. The pyrithione molecule as such, can be photolysed at wavelengths between 320-355 nm (Neihof et al., 1979), or degraded by chemical or biological oxidation (Turley et al., 2000).

Reported half-lives of zinc pyrithione and the cuprous counterpart vary from minutes to hours in water, whereas no studies have been made in sediments. In an artificial-light study using simulated sun light e.g. polychromatic light and artificial sea water the half-life of zinc pyrithione was 13-18 minutes and no traces of the compound could be detected after 30 days (Hanze et al., 2001). However, the complexes are thought to be stored in the aquatic environment as stable manganese or iron complexes (Galvin et al., 1998). It has further been shown that photodecomposition requires a pH < 6 and only the un-dissociated fraction of pyrithione (pKa = 4.6) is subject to photolysis (Galvin et al., 1995). However, photolysis half-lives between 15 min and > 10 days for depths up to 3 m have been presented at the 10^{th} International Congress on Marine Corrosion and Fouling (Turley et al., 1999).

Considering that the neutral fraction of pyrithione is < 0.1% at pH 8 and, based on the assumption that the partitioning of the pyrithione anion exclusively partitions to the water phase, the distribution constant log Dow is expected to be < -2. Therefore, it is expected that zinc pyrithione mainly occurs in the water phase under alkaline conditions (pH>7).

4 Use, regulations and emissions

Zinc pyrithione is an anti-fungal agent best known for its use in treating dandruff and seborrheic dermatitis. It was fist synthesized in the 1930's. Zinc pyrithione also has antibacterial properties and is effective against many pathogens from the streptococcus and staphylococcus class. Other medical uses involve treatment of skin conditions such as psoriasis, eczema, ringworm, fungus, athlete's foot, dry skin.

Due to its solubility in water (see above), zinc pyrithione is suitable for use in outdoor paints and other products that provide protection against mildew and algae. It is an effective algaecide. However, it is chemically incompatible with paints relying on metal carboxylate curing agents. The ban on tri-butyl-tin (TBT) in anti-fouling paints for pleasure boats in all the Nordic countries has resulted in the use of other booster biocides such as irgarol 1051, Sea-nine 211 and zinc pyrithione (Brady, 2000).

Zinc pyrithione is also approved for over-the-counter topical use in Sweden as a treatment for dandruff. It is the active ingredient in several anti-dandruff shampoos. However, in its industrial forms and strengths, it may be harmful by contact or ingestion.

Both zinc pyrithione and irgarol 1051 are considered to be biocides and the use of biocides is regulated within the European Union's biocide directive (98/8/EG). The directive has been implemented in the national Swedish legislation by the regulation 2000:338 on biocides. Within the framework of the directive 98/8/EC, each member state of the European Union can use national legislation until the year 2010 and Sweden is now acting to comply with the national objective of "Giftfri Miljö" (*eng.* A non-toxic environment).

Among bio-fouling components and products, only those that have a chemical mode of action need approval by the Swedish Chemicals Agency (Sv; KemI). If the product is considered to have a physical mode of action in the context of anti-fouling, no approval is needed. Furthermore, chemically active antifouling products are divided into three different classes depending on the chemicals included. If the antifouling products are classified by the Swedish Chemicals Agency as class 1- or class 2 products, they are only allowed to be used on boats and ships used for professional purposes (fishing, transportation etc) with a length exceeding 12 meters. The class 3-products can be used by everyone (i.e., boats used for recreational purposes).

The different anti-fouling products containing zinc pyrithione or irgarol 1051 currently approved by the Swedish Chemicals Agency are listed in Table 5. As can be seen from the table, zinc pyrithione-containing antifouling products are not allowed to be used for recreational boats, whereas irgarol-containing products can be found in both classes. The product names as such are of no interest in this report while the concentrations of the biocides in these products give an indication of the size and type of emission attributed to these products.

Table 5. Antifouling products containing zinc pyrithione and irgarol 1051 approved in Sweden.

Product	**Registry # (KemI)**	**Concentration (% w/w)**	**Classification**
Zinc pyrithione			
Hempel's Antifouling Combic ALU 71800	4481	4.1	2
Intersmooth 360 Spc	4480	4.3	2
Intersmooth 460 Spc	4479	4.3	2
Sanitized PL 21-60	4643	24	2
Trilux 33	4594	3.57	2
Irgarol 1051			
Antifouling Sargasso AL KNM	4223	2	2
Cruiser	4334	2.41	3
Cruiser White	4337	1.89	3
Hempel's Antifouling Combic ALU 71800	4481	1.1	2
Interspeed Extra BWO 500 Röd	3931	2	2
Interspeed Premium Antifouling Black	4296	2.3	2
Micron WQ	4333	2.2	3
Micron WQ White	4336	1.97	3
Mille White SE	4369	3.5	3
Trilux	4335	2.18	3
Trilux Prop-o-Drev	3914	0.87	3
Trilux White	4338	1.87	3
VC 17 New Technology	4116	0.6	3

There is no data available on the total use of irgarol 1051 in Sweden. For zinc pyrithione the Swedish Chemicals Agency (KemI) estimates that approximately 500 kg of the substance is being used annually (figures from 2004 and 2005, KemI). Estimated data from previous years are classified (1999-2003, KemI).

Regarding the use of zinc pyrithione in anti-dandruff products (i.e. shampoos etc) the Swedish Society for Nature Conservation (SNF) contacted the companies that sell shampoo products. These companies were asked whether they could consider disclosing information about market shares for their dandruff shampoo. All manufacturers but three answered and the concluding estimate made by the SNF yielded that at least 10 tonnes of zinc pyrithione was used in anti-dandruff products in Sweden 2003. SNF assumed that the density of anti-dandruff shampoo is 1.1 kg/litre and that the average zinc pyrithione concentration in a shampoo is 0.8 % (w/w). In the same report, the total amount of zinc pyrithione in antifouling products during 2003 was estimated to be 2.4 tonnes (SNF, 2004). Thus, it occurs as if the estimates done by KemI significantly underestimate the annual use of zinc pyrithione.

5 Previous investigations in the environment

Zinc pyrithiones and other metal pyrithiones have seldom been determined in environmental samples, presumably due to the rapid photolysis rendering it difficult to detect this type of compounds (Neihoff et al., 1979, and Galvin et al., 1995). However, in a study performed in Vietnam on sediments and clams, pyrithiones were detected in some of the samples in concentrations between <2-420 μg/kg dw. The corresponding concentration of irgarol 1051 in sediments was 0.05–4.0 μg/kg dw. Irgarol 1051 was never detected in the clam samples (Harino et al., 2006).

In an investigation performed in 2004 and commissioned by the Swedish Chemicals Agency, copper, zinc, and irgarol 1051 was determined in water, sediment, and bladderwrack (Sv. blåstång, *Fucus vesiculosus*) samples around Bullandö Marina in the Stockholm Archipelago (KemI, 2006). The bladderwrack was considered to be an integrating sampler of pollutants in the water over time, while water samples in themselves only gave a momentary picture of the concentrations. The sampling was carried out at four different sites: 1) a marina, 2) the sound outside the marina, 3) a natural harbour (frequented by pleasure boats), and 4) a background station. Water samples were taken periodically from the beginning of April until the beginning of November, while sediment and bladderwrack were sampled three times during this period. The metals were determined in all three types of samples, while irgarol 1051 was determined in water and bladderwrack only.

The water contained markedly higher concentrations of all three analytes in the marina (copper; 1.52-6.62 μg/l, zinc ; 2.73-20.0 μg/l, irgarol 1051; <0.005-0.17 μg/l) and in the natural harbour compared to the background station (copper; 0.72-1.74 μg/l, zinc; 0.64-2.19 μg/l, irgarol 1051; <0.005-0.008 μg/l). The levels, at least of zinc and irgarol 1051, also seem higher in the sound outside the marina than at the background station.

The concentrations in bladderwrack, similar to the water samples, indicated that the marina and the natural harbour were all affected by the boating activity (copper; 5-10 mg/kg, zinc; 300-799 mg/kg, irgarol 1051; 40-96 μg/kg). Also the samples from the sound outside the marina seemed to have elevated levels.

A comparison with a previous investigation from the same area conducted in 1993 shows that the levels of copper and zinc had increased since then in all types of samples and at all sites for which comparisons are possible. In the water samples, the copper concentrations had generally doubled, while zinc concentrations had increased with 650 %. Irgarol 1051 was not measured in the water samples in 1993. In bladderwrack the copper levels were ~1.5-2 times higher in 2004 than in 1993, while the irgarol 1051 levels were about half of those in 1993. Zinc was not measured in bladderwrack in 1993 (KemI, 2006). Notable is the fact that other anti-fouling chemicals than zinc pyrithione, such as zinc oxide, may contribute to the detected zinc concentrations.

In a Dutch investigation on antifouling substances, irgarol 1051 was frequently detected in estuarine and coastal water samples as well as in the corresponding sediments. The highest concentrations found in this investigation were 0.19 μg/l in the free water column and 1.7 μg/l in the ports and harbours. Like the Swedish study from the Stockholm archipelago, a clear seasonal trend was observed in the Dutch investigation; with maximal concentrations in the late spring-early summer, which corresponds very well with the start of the 'boating season' (van Wezel et al., 2001).

Irgarol 1051 has also been detected in the Mediterranean Côte d'Azur coastal waters where the concentration was 0.64 μg/l (Tolosa et al., 1993).

6 Sampling programmes and study sites

6.1 National sampling programme

A sampling strategy for the screening was developed in order to determine the environmental concentrations of zinc pyrithione and irgarol 1051 in different environmental matrices in Sweden. An additional aim of the sampling programme was to identify major emission sources as well as important transport pathways. The sampling programme was based on identified possible emission sources and the behaviour of the substances in the environment. The sampling programme is summarised in Table 6. Site information and sample characteristics of the samples collected within the national programme are given in Appendix 1.

The sampling programme takes into account both the use of zinc pyrithione in hygienic products such as anti-dandruff shampoos, and the use of zinc pyrithione (and irgarol 1051) as chemically active antifouling compounds.

One possible point source was identified in "Falun/Borlänge" (Table 6). These samples are process waters from a cosmetics producer in Falun (producing anti-dandruff shampoo) that redirects all used process- and sewage water to the STP in Borlänge by tank lorry. From this "point source" three water samples were collected; one process water sample directly from the tank lorry, one effluent water sample, and one sludge hydration reject water sample. The sites selected at the Swedish west coast, where possible contamination was suspected, have been denoted "affected areas" rather than "point sources" since the samples cover a rather extended stretch of the coast having a high frequency of small harbours, marinas, boat clubs and professional fishermen. Biota samples from the "affected areas" are in fact mussels originating from a sampling position in Brofjorden, in the vicinity of an oil refinery plant with a harbour with frequent traffic.

In order to cover diffusive sources in an urban area (Stockholm) surface water, sediment and biota were collected at the point where the effluents from the Henriksdal- and the Bromma STPs are emitted into Saltsjön (between Stadsgården, Kastellholmen and Skeppsholmen). As a reference point for these two STP outlets a third sample was collected outside the Wasa museum (approximately 1 km from the point where the STP effluents reach Saltsjön). Samples from municipal sewage treatment plants (STPs) were also collected, as they were identified as important sources for the occurrence of the compounds in the aquatic environment. STP samples e.g. sludge, are often used as indicators for diffuse spreading of chemicals to the environment.

In order to obtain reference levels in water, sediments and biota, samples representing these matrices were taken from six different "background" lakes where the influence from human activities was considered minor.

Urine samples were analysed in order to investigate the potential for human exposure.

Table 6. National sampling programme.

Source	Site	Surface water	Sediment	Influent-/Effluent Water	Sludge	Biota	Urine	Total
Background	Lake Gårdsjön	1						1
	Tärnan	1						1
	Härsevatten	1						1
	Krageholmsjön		1			1		2
	Lilla Örsjön		1			1		2
	Övre Skärsjön		1			1		2
Point Sources/Affected areas								
	West coast		3			6		9
	Falun/Borlänge			3	1			4
Diffuse source								
Urban Stockholm								
	Riddarfjärden	1	1			1		3
	St.Essingen	1	1			1		3
	Årstaviken	1	1			1		3
	STPs Sthlm	3	3	3	2	3		14
	*SEPAMPEPS				4			4
Human exposure							6	6
Total		9	12	6	7	15	6	55

* SEPAMPEPS = Swedish Environmental Protection Agency's Monitoring Program for Environmental Pollutants in Sludge

6.2 Regional sampling programmes

Swedish county administrative boards had the possibility to add "regional" samples (74 altogether) to the national sampling programme. The main focus in the regional screening programme was to take samples from STPs. A majority of samples were taken from sludge (27 samples). Effluent- and influent water samples were both considered interesting (16 effluent samples, 17 influent samples). In addition, also 4 sediment samples were submitted to the programme, taken from areas with harbours and boat clubs. At three sites in the south of Sweden, drinking water was sampled in combination with the raw water used for the production of drinking water (directly from the water reservoir). In total eight regional county administrative boards participated in the regional screening programme.

Detailed information about sampling sites and sample characteristics of the samples included in the regional programme are given in Appendix 2

7 Methods

7.1 Sampling

The overall most important instruction regarding sampling within the zinc pyrithione programme, emphasized in all sampling instructions, was that all samples (regardless of matrix) were to be safeguarded from light exposure. All vessels containing sampled material were to be immediately covered in light reflecting aluminium foil in order to minimise photolysis of the metal pyrithione complexes. During sampling of solid matrices, i.e., sediment and sludge, the sampling personnel were instructed to utilise plastic tools rather than steel tool, in order to avoid contact contamination. As a guideline for adequate and consequent sampling, a manual for the sampling personnel in the national as well as the regional screening programs was developed. Detailed instructions for sampling, storing and transport were outlined. 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.

Water samples were collected in cleaned plastic bottles and stored 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. Sediment samples from lakes were collected by means of a Kajak sampler. The sediment core was sliced and transferred into plastic jars and stored until analysed. A plastic jar filled with diatomaceous earth (10 % water) that was exposed to the surrounding environment during the sampling time was used as field blank. Sludge samples were collected from the anaerobic chambers by the staff at the different treatment plants. The sludge was transferred into plastic jars and stored at 4°C or -18°C until analysed. A plastic jar filled with diatomaceous earth (10 % water), which was exposed to the surrounding environment during the sampling, was used as a field blank.

7.2 Analytical methods

The method of extraction and analysis of zinc pyrithione and irgarol 1051 was modified from Bones et al (2006). Since the Zn-pyrithione (ZPT) is easily degraded by daylight the samples were safeguarded from light exposure (daylight and fluorescent lighting) during the extraction procedure and the following clean-up and analysis process.

7.2.1 Extraction

Water samples were acidified (pH 2) and extracted onto Oasis HLB SPE cartridges. Elution was performed by 4 ml DCM. 1 ml of extract was removed for Irgarol 1051 analysis and 2 ml methanol added to the remaining extract that was used for the analysis of ZPT.

Sludge and sediment samples to be analysed for zinc pyrithione were air dried before extraction. 3-gram aliquots were subjected to ultrasonic extraction with 30 ml DCM:Methanol (2:1) for 45 minutes. After centrifugation (3500 rpm, 10 mins) extracts were filtered (0.45 µm GFC) before addition of 2 ml methanol.

Sludge and sediment samples which were to be analysed for irgarol 1051 were spiked with recovery standard (d5-oxasepam) homogenised and extracted with a mixture of methanol and acetonitrile (1+1) according to Ramirez et al (2007). The extracts were centrifuged and evaporated prior to LC-MS analysis.

7.2.2 HPLC-MS Analysis

Extracts which were to be analysed for zinc pyrithione were evaporated to approximately 1 ml under nitrogen and made up to 50 ml with ultrapure water prior to loading on the guard column. An Onyx Monolithic C_{18} guard cartridge (Phenomenex UK) was conditioned at 5 ml/min with 10 ml methanol and 10 ml water prior to loading with 50 ml sample extracts. Matrix interference was reduced by an anion exchange silica column positioned before the extraction guard column; this was back flushed with methanol between samples. The guard column was then flushed onto a Chromolith monolithic column (Merck, Norway) by gradient elution (methanol-ammoniumacetate) and the ZPT detected by dual electro spray chemical ionisation in positive mode mass spectrometry in selected ion monitoring mode. The ions detected were m/z 221, 316, 317, 318, 319, 321.

For samples, which were to be analysed for irgarol 1051, liquid chromatography was performed with an Agilent 1100 liquid chromatography system (Agilent Technologies, Waldbronn, Germany), equipped with an autosampler, a quaternary pump, an on-line degassing system and a diode array detector (UV). The compound separation was performed with a reversed phase C_{18}-column (Atlantis dC_{18}, 2.1 mm ID x 150 mm length, 3 µm, Waters, Milford USA). The analytical detector was a Micromass LCT orthogonal-acceleration time-of-flight (TOF) mass spectrometer (MS) equipped with a Z-spray electrospray ion source and a 4 GHz time to digital converter (TDC) (Micromass Ltd., Wythenshawe, Manchester, UK). Electro spray ionization (ESI) was used in positive ion mode. The data processing and instrument (HPLC/HRMS) control were performed by the MassLynx software. The monitoring ion was m/z 254 with 198.5 as a qualifier.

7.2.3 Analysis of Zn(tot) and Pb(tot)

Solid samples and urine
Up to 1 g sample material was weighted into Teflon vessels, and 3 ml H_2O_2 and 5 ml HNO_3 was added. The Teflon vessels were closed and the sample material digested in a microwave oven. After digestion, the samples were diluted to 20 or 100 ml using MilliQ water. Before analysis on the ICP-HR-MS, 1 ppb Rhenium (Re) was added to the samples, as internal standard. Zn in the samples was determined by monitoring ^{64}Zn in medium and high resolution using a ICP-HR-MS, whereas Pb was determined by monitoring and ^{208}Pb in low resolution.

Aqueous samples
Before analysis, 1 ppb Rhenium (Re), which served as internal standard, was added to the samples. The samples were then acidified by addition of HNO3 (1 % vol/vol in the resulting sample). Zn and Pb in the samples were determined by monitoring ^{64}Zn and ^{208}Pb respectively in medium and high resolution using a ICP-HR-MS. The measurements were conducted on a Thermo Element 2 ICP-HR-MS.

8 Results and discussion

The concentrations of zinc pyrithione found in the different samples from the national and regional screening are given in tabular form in Appendix 1 and Appendix 2, along with the corresponding irgarol 1051-, Zn- and Pb- concentrations. In the discussion, focus has been put on analysing concentration patterns of irgarol 1051, and when present, zinc pyrithione. Because of the very scarce occurrence of zinc pyrithione in environmental samples, it was not possible to elucidate any correlation of this substance with zinc. The occurrence of the metals Zn and Pb has not been commented to any further extent as the study was designed for tracking the anti-fouling substances. Data are presented however, and may serve as a good additional data source for Zn and Pb levels in the environment.

As mentioned above, the detection frequency of zinc pyrithione was generally low. Detection limits varied depending on the complexity of the sample, but the average detection limits for the various substances in different matrices are shown in Table 7.

Table 7. Detection limits in various matrices for the substances included in the screening

Substance	Water (µg/L)	Sludge (µg/kg dw)	Sediment (µg/kg dw)	Fish (ng/g ww)	Urine (µg/l)
Zn-pyrithione	0.015	20	20	-	0.05
Irgarol 1051	0.0003	1	0.001-1	1	0.0003
Zn	0.05	0.1	0.25	120	1.3
Pb	0.005	0.05	0.05	2.0	0.11

8.1 Water

Zinc pyrithione was only detected in three water samples; two representing STP influents (Jämshögs STP in Olofström 1.9 µg/l and Askersunds STP in Örebro, 17 µg/l) and in one effluent water sample from a hospital (Karlskrona Hospital; 32 µg/l). This hospital does not have any treatment system of its own, but is affiliated with the local municipal STP, and as such it can be regarded as an influent sample to the local STP rather than an effluent sample. The levels of zinc pyrithione were below the detection limit in all other water samples (Table 7).

The levels of irgarol 1051, Zn and Pb found in the analysed water samples are shown in Figure 1. It should be noted that in three of the samples indicated in the figure, irgarol 1051 was not analysed. This concerns the leachate sample from Bubbetorp landfill, and two influent samples from Skebäck and Mörrums STP. Other data gaps in the figure indicate that the level was below the detection limit (see Table 7). Irgarol 1051 was detected in six samples of incoming sewage water, 13 effluent samples and in three samples of urban surface water. It was not found in background water samples. The metals were, not surprisingly, found in all the analysed samples.

It is very difficult to draw any conclusions from these data as to whether the total contents of zinc in any way reflects the presence of dissociated zinc pyrithione, mainly because of the low detection frequency of zinc pyrithione. Also, the Karlskrona hospital sample which did contain detectable amounts of zinc pyrithione contained zinc levels in similar order of magnitude as in other STP influent water samples, where zinc pyrithione was below the detection limit.

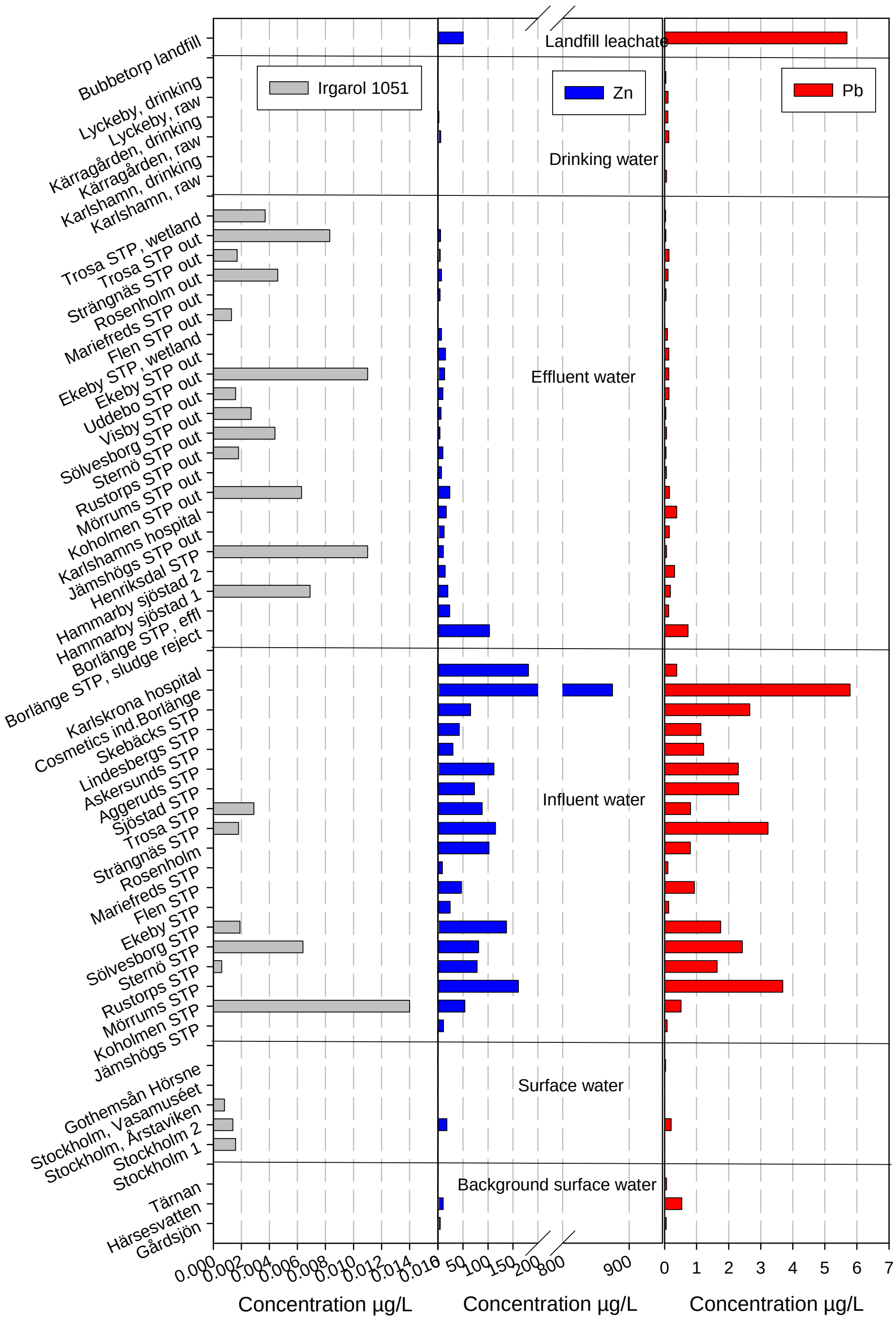


Figure 1. Contents of irgarol 1051, Zn and Pb in water samples. Irgarol 1051 was not analysed in the sample from Bubbetorp landfill, nor in the influent samples from Skebäck and Mörrums STP.

8.2 Sludge

Sludge samples from 34 STPs were analysed with respect to zinc pyrithione and irgarol 1051. Zinc pyrithione was not detected in any of the samples (LOD< 20 µg/kg dw). 18 of the sludge samples contained irgarol 1051 in concentrations above the LOD (< 1 µg/kg dw), with a median concentration of 5.5 µg/kg dw. The results are shown in Figure 2. Nykvarn and Slottshagen contained the highest levels of irgarol 1051 (54 and 48 µg/kg dw respectively). The concentrations of Zn and Pb detected in sludge are presented in Appendix 1 and Appendix 2.

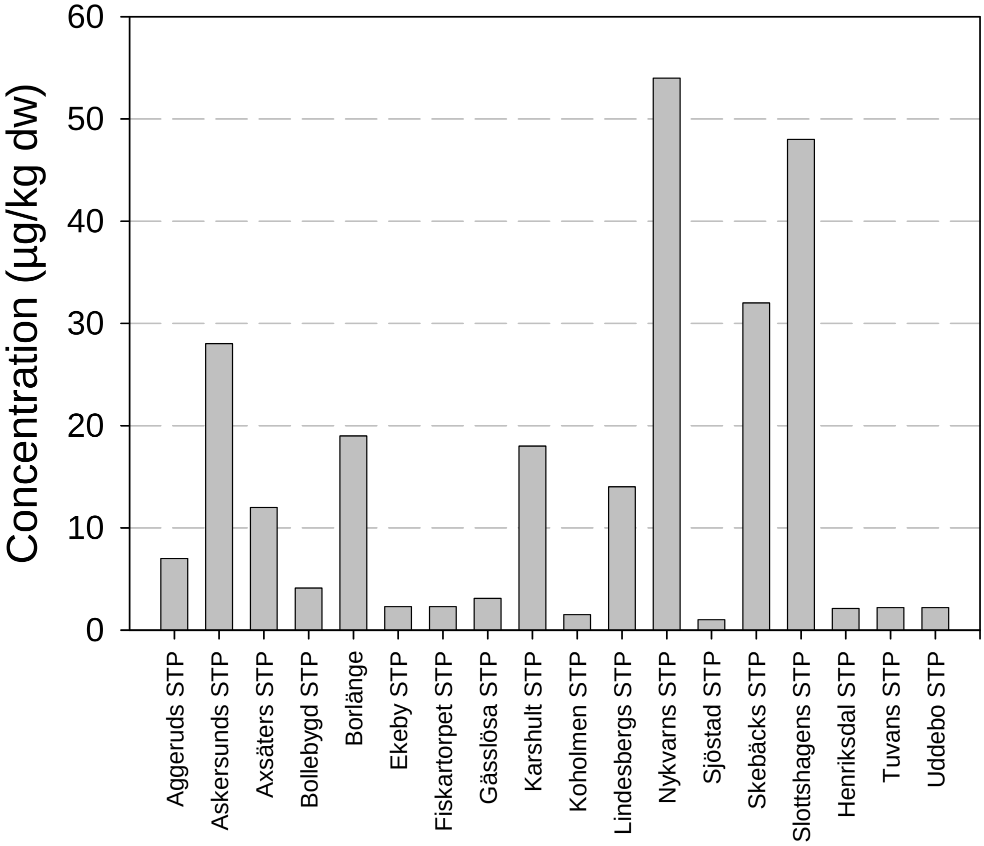


Figure 2. The contents of irgarol 1051 in sludge samples.

8.3 Sediment

Zinc pyrithione was not detected in the 16 analysed sediment samples (LOD < 20 µg/kg DW). Irgarol 1051 was found in 11 of the samples. The results are summarised in Figure 3. In general, the irgarol levels were slightly lower in the urban sediments as compared to sediments collected in harbour areas. Surprisingly, the irgarol levels in sediment varied substantially between Bromma STP and Henriksdal STP, which both emit their effluent to the same area in Saltsjön. It is possible, that the difference between the detected levels is merely a result of natural variation in the sediment composition. The concentrations of Zn and Pb detected in sediment are presented in Appendix 1 and Appendix 2.

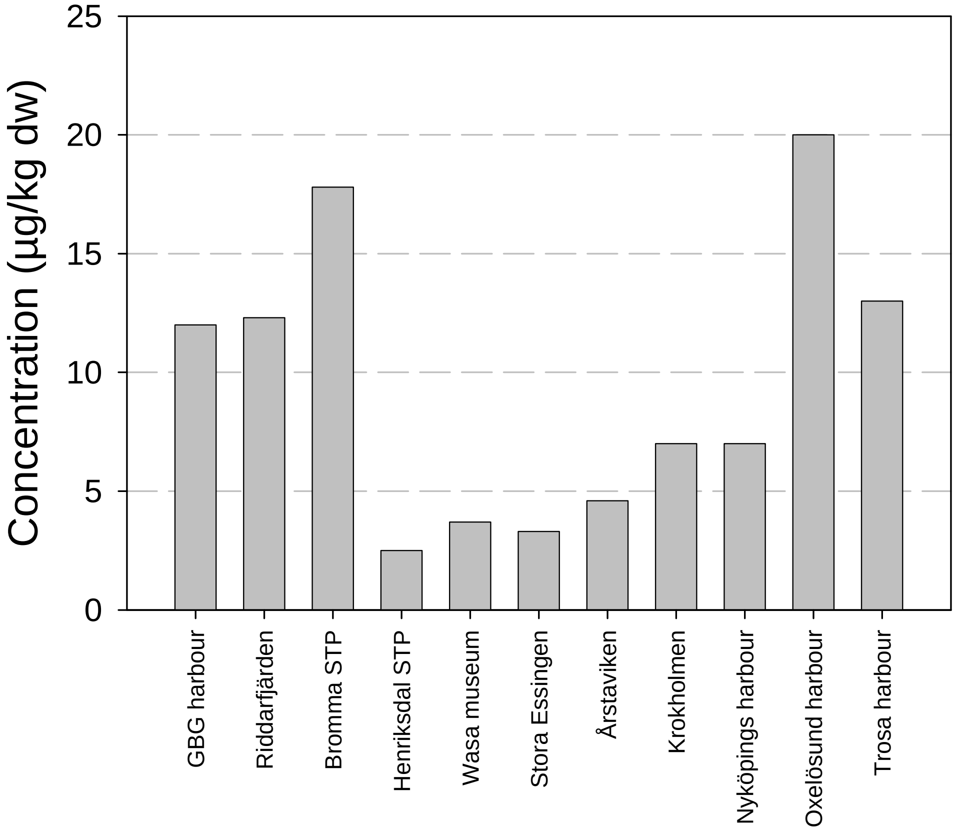


Figure 3. The contents of irgarol 1051 in sediment samples. The "STP" samples were taken in the recipient just outside the STP effluent point.

8.4 Biota – Fish and Mussels

Irgarol 1051 was not detected (LOD < 1 ng/g ww) in any of the fish samples analysed. (The results of zinc pyrithione in biota will be given in an additional report.)

8.5 Human exposure

Zinc pyrithione was not detected in the human urine samples. The LOD in urine samples was determined to be 0.05 µg/l. Five of the included urine samples did not show any traces of zinc pyrithione while in one sample analytical interference problems precluded any determination of zinc pyrithione. The metal content in the analysed urine samples is shown in Figure 4.

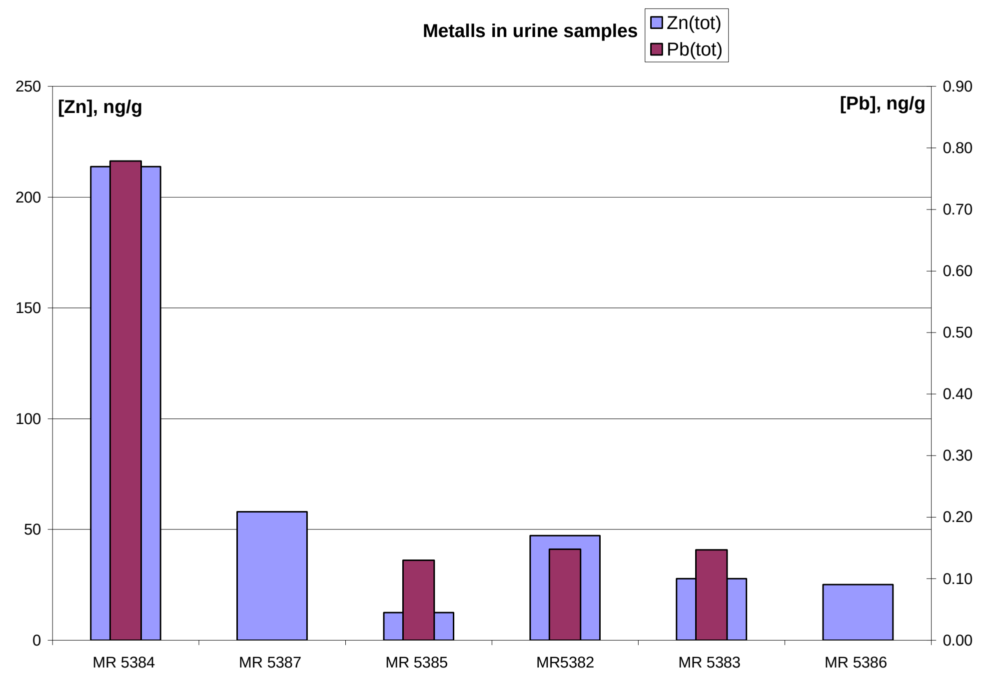


Figure 4. The contents of Lead (Pb) and Zinc (Zn) in urine samples.

9 Conclusions

The following conclusions can be drawn from this screening study:

- Zinc pyrithione was only detected in three environmental samples, thus it is not regarded as problematic substance; no further monitoring is necessary.
- It was not possible to identify any correlation between zinc and zinc pyrithione.
- The limited detection frequency despite extensive use indicate high degradation rate of zinc pyrithione
- Irgarol 1051 was detected in approximately 70 % of all sediment samples (from all sampling sites apart from the background sites). This is not surprising considering the use of the substance as an antifouling component in boat paints. However irgarol 1051 was also detected in approximately 50 % of the sludge samples, suggesting; 1) a wide use of the substance throughout Sweden, and 2) other sources and usage applications of the substance than previously reported.
- Irgarol 1051 was more frequently occurring in STP effluent water, than in ingoing water. The reason for this is unclear.
- In three cases are the influent concentrations of irgarol 1051 higher than the corresponding effluent concentration from the very same STP (Koholmen, Sternö, and Strängnäs), and in six cases are the corresponding effluent concentrations of irgarol 1051 higher than the influent concentrations (Trosa, Rosenholm, Flen, Sölvesborg and Rustrop).
- Sediment and sludge seem to be appropriate matrices to analyse with regard to irgarol 1051.
- Neither irgarol 1051 nor zinc pyrithione occurred in humane urine

10 Acknowledgements

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Appendix 1. National sample programme

MR-nr	Type	Matrix	Site	Information	DW. %	Unit	Zn pyrithione	Irgarol 1051	Zn(tot)	Pb(tot)
5654	Background	Fish	Gårdsjön			µg/kg ww			3 000	25
	Background	Fish	Gårdsjön			µg/kg ww			-	-
	Background	Fish	Gårdsjön			µg/kg ww			-	-
5243	Background	Fish	Krageholmssjön	perch		µg/kg ww		< 1	5 000	22
5244	Background	Fish	Lilla Öresjön	perch		µg/kg ww		< 1	4 500	21
5245	Background	Fish	Övre Skärsjön	perch		µg/kg ww		< 1	3 190	3,5
5242	Background	Sediment	Krageholmssjön		21.2	µg/kg dw	<20	< 0.001	41 700	2 300
5241	Background	Sediment	Lilla Öresjön		30.1	µg/kg dw	<20	< 0.001	59 100	3 290
5240	Background	Sediment	Övre Skärsjön		37.8	µg/kg dw	<20	< 0.001	27 800	783
5642	Background	Water	Gårdsjön	Surface water	-	µg/l	<0.015	<0.0003	4.25	0.053
5643	Background	Water	Härsesvatten	Surface water	-	µg/l	<0.015	<0.0003	10.2	0.54
5563	Background	Water	Tärnan	Surface water	-	µg/l	<0.015	<0.0003	0.61	0.062
5536	Affected area	Sludge	Borlänge		36.2	µg/kg dw	<20	19	474 000	10 500
5532	Affected area	Water	Borlänge STP	Sludge Reject water	-	µg/l	<0.04	<0.0003	103	0.734
5533	Affected area	Water	Borlänge STP	Effluent	-	µg/l	<0.015	<0.0003	23.3	0.130
5534	Affected area	Water	Cosmetcs industry, infl. to Borlänge STP	Effluent	-	µg/l	<0.3	<0.0003	875	5.79
5401	Affected area	Sediment	GBG harbour		41.5	µg/kg dw	<20	<1	35 700	6 790
5402	Affected area	Sediment	GBG harbour		42.6	µg/kg dw	<20	<1	29 100	6 130
5411	Affected area	Sediment	GBG harbour		28.4	µg/kg dw	<20	12	45 100	8 120
5529	Diffuse	Fish	Stockholm (STP)			µg/kg ww		< 1	4 890	13
5530	Diffuse	Fish	Stockholm (STP)			µg/kg ww		< 1	5 100	3.0
5531	Diffuse	Fish	Stockholm (STP)			µg/kg ww		< 1	6 900	3.0
5526	Diffuse	Fish	Stockholm, Riddarfjärden			µg/kg ww		< 1	4 500	4.0
5527	Diffuse	Fish	Stockholm, Stora Essingen			µg/kg ww		< 1	6 000	11
5528/4492	Diffuse	Fish	Stockholm, Årstaviken			µg/kg ww		< 1	6 500	6.0

MR-nr	Type	Matrix	Site	Information	DW. %	Unit	Zn pyrithione	Irgarol 1051	Zn(tot)	Pb(tot)
5296	Diffuse	Sediment	Riddarfjärden		41.3	µg/kg dw	<20	12.3	46 000	1 890
5297	Diffuse	Sediment	Stockholm (Bromma STP, near outflow)		53.7	µg/kg dw	<20	17.8	139 000	5 320
5298	Diffuse	Sediment	Stockholm (Henriksdal STP, near outflow)		38.4	µg/kg dw	<20	2.5	114 000	62 200
5502	Diffuse	Sediment	Stockholm (Vasamuséet)		69.2	µg/kg dw	<20	3.7	60 600	7 160
5287	Diffuse	Sediment	Stora Essingen		72.9	µg/kg dw	<20	3.3	9 780	492
5288	Diffuse	Sediment	Årstaviken		67.7	µg/kg dw	<20	4.6	6 880	187
5078	Diffuse	Sludge	Stockholm, Hammarby sjöstad		39.3	µg/kg dw	<20	< 1	168 000	6 560
5075	Diffuse	Sludge	Stockholm, Henriksdal, Sickla		51.8	µg/kg dw	<20	2.1	243 000	13 400
5294	Diffuse	Water	Stockholm	Surface water	-	µg/l	<0.015	0.0016	0.36	0.017
5295	Diffuse	Water	Stockholm	Surface water	-	µg/l	<0.015	0.0014	17.7	0.206
5291	Diffuse	Water	Stockholm, Årstaviken	Surface water	-	µg/l	<0.015	0.0008		
5076	Diffuse	Water	Stockholm, Hammarby sjöstad	Effluent	-	µg/l	<0.015	0.0069	19.8	0.184
5077	Diffuse	Water	Stockholm, Hammarby sjöstad	Effluent	-	µg/l	<0.015	<0.0003	14.2	0.314
5074	Diffuse	Water	Stockholm, Henriksdal, Sickla	Effluent	-	µg/l	<0.015	0.011	10.4	0.059
5501	Diffuse	Water	Stockholm, Vasamuséet	Surface water	-	µg/l	<0.015	<0.0003		
5226	Diffuse	Sludge	Ellinge STP, Eslöv	126 000 p e	34.0	µg/kg dw	<20	< 1	216 000	7 200
5227	Diffuse	Sludge	Gässlösa STP, Borås	110 000 p e	44.0	µg/kg dw	<20	3.1	262 000	9 200
5223	Diffuse	Sludge	Nolhaga STP; Alingsås,	24 000 pe	53.0	µg/kg dw	<20	<1	182 000	8 670
5225	Diffuse	Sludge	Bollebygd STP	2 200 p e	32.0	µg/kg dw	<20	4.1	151 000	3 330
5382	Human expo.	Urine				µg/l	< 0.05	<0.001	48	0.15
5383	Human expo.	Urine				µg/l	-*	<0.0003	28	0.15
5384	Human expo.	Urine				µg/l	< 0.05	<0.0003	214	0.78
5385	Human expo.	Urine				µg/l	< 0.05	<0.0003	13	0.13
5386	Human expo.	Urine				µg/l	< 0.05	<0.0003	25	< 0.11
5387	Human expo.	Urine				µg/l	< 0.05	<0.0003	58.	< 0.11

*Analytical interference problems prevented determination of zinc pyrithione

Appendix 2. Regional sample programme

MR-nr	County	Site	Information	Matrix	DW. %	Unit	Zn pyrithione	Irgarol 1051	Zn(tot)	Pb(tot)
5041	Blekinge (K)	Bubbetorp deponi	Landfill leachate	Water	-	µg/l	<0.015		50.5	5.69
5249	Blekinge (K)	Jämshögs STP		Sludge	43.3	µg/kg dw	<20	< 1	202 000	4 060
5246	Blekinge (K)	Jämshögs STP	Influent	Water	-	µg/l	1.9	<0.0003	10.7	0.08
5247	Blekinge (K)	Jämshögs STP	Effluent	Water	-	µg/l	<0.015	<0.0003	11.9	0.149
5482	Blekinge (K)	Karlshamns sjukhus	Effluent	Water	-	µg/l	<0.015	<0.0003	16.4	0.381
5054	Blekinge (K)	Karlshamns WW	Raw water (Mieån)	Water	-	µg/l	<0.015	<0.0003	1.23	0.061
5056	Blekinge (K)	KarlshamnsWW	Drinking water	Water	-	µg/l	<0.015	<0.0003		
5279	Blekinge (K)	Karlskrona sjukhus	Effluent	Water	-	µg/l	32	<0.0003	181	0.379
5044	Blekinge (K)	Koholmen STP		Sludge	35.3	µg/kg dw	<20	1.5	95 300	5 520
5042	Blekinge (K)	Koholmen STP	Influent	Water	-	µg/l	<0.015	0.014	53.8	0.514
5043	Blekinge (K)	Koholmen STP	Effluent	Water	-	µg/l	<0.015	0.0063	23.6	0.154
4978	Blekinge (K)	Kärragårdens WW	Raw water (Listerån)	Water	-	µg/l	<0.015	<0.0003	5.34	0.131
4979	Blekinge (K)	Kärragårdens WW	Drinking water	Water	-	µg/l	<0.015	<0.0003	1.68	0.107
5046	Blekinge (K)	Lyckeby WW	Raw water (Lyckebyån)	Water	-	µg/l	<0.015	<0.0003	0.87	0.11
5047	Blekinge (K)	Lyckeby WW	Drinking water	Water	-	µg/l	<0.015	<0.0003	0.75	0.045
5034	Blekinge (K)	Mörrums STP		Sludge	52.3	µg/kg dw	<20	< 1	165 000	5 660
5031	Blekinge (K)	Mörrums STP	Influent	Water	-	µg/l	<0.015	<0.0003	161	3.69
5032	Blekinge (K)	Mörrums STP	Effluent	Water	-	µg/l	<0.015	<0.0003	6.78	0.057
4983	Blekinge (K)	Rustorps STP		Sludge	46.0	µg/kg dw	<20	< 1	142 000	5 470
4981	Blekinge (K)	Rustorps STP	Influent	Water	-	µg/l	<0.015	0.0006	78.0	1.64
4982	Blekinge (K)	Rustorps STP	Effluent	Water	-	µg/l	<0.015	0.0018	9.42	0.048
5024	Blekinge (K)	Sternö STP		Sludge	53.1	µg/kg dw	<20	< 1	200 000	9 460
5021	Blekinge (K)	Sternö STP	Influent	Water	-	µg/l	<0.015	0.0064	81.3	2.43
5022	Blekinge (K)	Sternö STP	Effluent	Water	-	µg/l	<0.015	0.0044	3.77	0.060
5263	Blekinge (K)	Sölvesborg STP		Sludge	36.2	µg/kg dw	<20	< 1	109 000	1 790

MR-nr	County	Site	Information	Matrix	DW. %	Unit	Zn pyrithione	Irgarol 1051	Zn(tot)	Pb(tot)
5260	Blekinge (K)	Sölvesborg STP	Influent	Water	-	µg/l	<0.015	0.0019	137	1.75
5261	Blekinge (K)	Sölvesborg STP	Effluent	Water	-	µg/l	<0.015	0.0027	6.04	0.043
5071	Dalarna (W)	Fagersta By STP		Sludge	47.3	µg/kg dw	<20	< 1	307 000	11 100
5108	Gotland (I)	Gothemsån Hörsne	Surface water	Water	-	µg/l	<0.015	<0.0003	0.67	0.034
5109	Gotland (I)	Visby STP	Effluent	Water	-	µg/l	<0.015	0.0016	9.72	0.139
5082	Norrbotten (BD)	Uddebo STP		Sludge	35.1	µg/kg dw	<20	2.2	170 000	4 030
5080	Norrbotten (BD)	Uddebo STP	Effluent	Water	-	µg/l	<0.015	0.011	12.9	0.132
5131	Södermanland (D)	Ekeby STP		Sludge		µg/kg dw	<20	2.3		
5133	Södermanland (D)	Ekeby STP	Influent	Water	-	µg/l	<0.015	<0.0003	24.3	0.130
5134	Södermanland (D)	Ekeby STP	Effluent	Water	-	µg/l	<0.015	<0.0003	14.9	0.133
5135	Södermanland (D)	Ekeby STP	Effluent, wetland	Water	-	µg/l	<0.015	<0.0003	6.85	0.089
4999	Södermanland (D)	Flen STP		Sludge	40.5	µg/kg dw	<20	<1	88 500	2 480
4996	Södermanland (D)	Flen STP	Influent	Water	-	µg/l	<0.015	<0.0003	46.9	0.929
4997	Södermanland (D)	Flen STP	Effluent	Water	-	µg/l	<0.015	0.0013		
5014	Södermanland (D)	Krokholmen		Sediment	25.4	µg/kg dw	<20	7	43 800	6 580
4973	Södermanland (D)	Mariefreds STP		Sludge	40.5	µg/kg dw	<20	< 1	153 000	4 560
4970	Södermanland (D)	Mariefreds STP	Influent	Water	-	µg/l	<0.015	<0.0003	8.87	0.107
4971	Södermanland (D)	Mariefreds STP	Effluent	Water	-	µg/l	<0.015	<0.0003	4.04	0.050
5017	Södermanland (D)	Nyköpings småbåtshamn		Sediment	31.2	µg/kg dw	<20	7	89 300	12 100
5015	Södermanland (D)	Oxelösund Fiskehamnen		Sediment	24.0	µg/kg dw	<20	20	153 000	85 700
5029	Södermanland (D)	Rosenholm		Sludge	49.0	µg/kg dw	<20	< 1	201 000	11 000
5026	Södermanland (D)	Rosenholm	Influent	Water	-	µg/l	<0.015	<0.0003	102	0.807
5027	Södermanland (D)	Rosenholm	Effluent	Water	-	µg/l	<0.015	0.0046	6.70	0.110
4976	Södermanland (D)	Strängnäs STP		Sludge	44.2	µg/kg dw	<20	< 1	160 000	8 870
4974	Södermanland (D)	Strängnäs STP	Influent	Water	-	µg/l	<0.015	0.0018	115	3.23
4975	Södermanland (D)	Strängnäs STP	Effluent	Water	-	µg/l	<0.015	0.0017	4.26	0.138
5052	Södermanland (D)	Trosa STP		Sludge	43.8	µg/kg dw	<20	< 1	132 000	3 820
5048	Södermanland (D)	Trosa STP	Influent	Water	-	µg/l	<0.015	0.0029	88.5	0.81
5049	Södermanland (D)	Trosa STP	Effluent	Water	-	µg/l	<0.015	0.0083	5.03	0.045
5050	Södermanland (D)	Trosa STP	Effluent, wetland	Water	-	µg/l	<0.015	0.0037	0.46	0.032

MR-nr	County	Site	Information	Matrix	DW. %	Unit	Zn pyrithione	Irgarol 1051	Zn(tot)	Pb(tot)
5016	Södermanland (D)	Trosa harbour		Sediment	34.5	µg/kg dw	<20	13	123 000	11 600
4994	Värmland (S)	Fiskartorpet STP		Sludge	50.4	µg/kg dw	<20	2.3	187 000	11 800
4989	Värmland (S)	Sjöstad STP		Sludge	58.2	µg/kg dw	<20	1.0	295 000	17 100
4986	Värmland (S)	Sjöstad STP	Influent	Water	-	µg/l	<0.015	<0.0003	73.0	2.31
5019	Värmland (S)	Vik STP		Sludge	41.0	µg/kg dw	<20	< 1	76 600	4 810
5038	Västerbotten (AC)	Lycksele STP		Sludge	42.5	µg/kg dw	<20	< 1	103 000	3 540
5039	Västerbotten (AC)	Tuvans STP		Sludge	32.2	µg/kg dw	<20	2.2	182 000	8 110
5067	Örebro (T)	Aggeruds STP		Sludge	1.6	µg/kg dw	<20	7	95 200	4 400
5066	Örebro (T)	Aggeruds STP	Influent	Water	-	µg/l	<0.015		112	2.30
5557	Örebro (T)	Askersunds STP		Sludge	98.2	µg/kg dw	<20	28	23 900	947
5556	Örebro (T)	Askersunds STP	Influent	Water	-	µg/l	17	<0.0003	29.9	1.22
5123	Örebro (T)	Lindesbergs STP		Sludge	21.5	µg/kg dw	<20	14	148 000	8 030
5121	Örebro (T)	Lindesbergs STP	Influent	Water	-	µg/l	<0.015	<0.0003	42.4	1.13
5127	Örebro (T)	Skebäcks STP		Sludge		µg/kg dw	<20	32	290 000	13 600
5126	Örebro (T)	Skebäcks STP	Influent	Water	-	µg/l	<0.015		65.1	2.66
5062	Östergötland (E)	Axsäters STP		Sludge		µg/kg dw	<20	12		
4969	Östergötland (E)	Karshult STP		Sludge		µg/kg dw	<20	18		
4967	Östergötland (E)	Nykvarns STP		Sludge	28.8	µg/kg dw	<20	54	299 000	31 300
4968	Östergötland (E)	Slottshagens STP		Sludge	24.6	µg/kg dw	<20	48	267 000	13 100