REPORT

Results from the Swedish National Screening Programme 2008

Subreport 1. Biocides: 3-Iodo-2-propynyl butyl carbamate (IPBC) and 2,2-dibromo-2-cyanoacetamide (DBNPA)

Karin Norström, Mikael Remberger, Lennart Kaj,
Per Wiklund, Eva Brorström-Lundén
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Lars-Gunnar Lindfors
Scientific Director

IVL Swedish Environmental Research Institute

IVL Swedish Environmental Research Institute

Organization

IVL Swedish Environmental Research Institute Ltd.

Address

Box 21060
100 31 Stockholm

Telephone

+46 (0)8-598 563 00

Report Summary

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Karin Norström Mikael Remberger, Lennart Kaj, Per Wiklund, Eva Brorström-Lundén

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Sammanfattning

IVL Swedish Environmental Research Institute has performed a "Screening Study" of IPBC and DBNPA as an assignment from the Swedish Environmental Protection Agency. IPBC belongs to the category preservatives/disinfectants and is used as a fungicide. It is used in the paper and pulp industry to prevent the formation of slime and as a preservative in cosmetics, paints, coatings etc. DBNPA is mostly used to reduce the occurrence of slime forming microorganisms with in the paper and cellulose industry. It is also used a biocide in cooling systems. IPBC is moderately soluble and not very persistent in water, hydrolysis is expected to be main route of dissipation. DBNPA has high water solubility, a short half-life and is rapidly degraded in water by hydrolysis. The overall objectives of the study were to determine the concentrations of IPBC and DBNPA in the Swedish environment. A sampling strategy was developed and the selection was based on the usage pattern of the substances. IPBC was found in air at two paint companies representing point sources and in the centre of Gothenburg, representing an urban diffuse source. In water, IPBC was found in high levels in the influent water at two paint companies and in both the in- and effluent water from three STPs. It was not found in background areas or in urban surface water, storm water and sediment, STP sludge or storm water sludge. The results indicate that if IPBC is being used, there is a possibility for the compound to be distributed to the environment since in can be detected in air and influent and effluent water from the paint industries and in STP waters. However, IPBC does not seem to reach other urban or background areas which may be due to the fact that IPBC is not very persistent in water. DBNPA was found below LOD in all samples.

Nyckelord samt ev. anknytning till geografiskt område eller näringsgren

IPBC, DBNPA, screening, point sources, background

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Hemsida: www.ivl.se, e-post: publicationservice@ivl.se, fax 08-598 563 90, eller via IVL, Box 21060, 100 31 Stockholm

Sammanfattning

IVL Svenska Miljöinstitutet AB har på uppdrag av Naturvårdsverket genomfört en screening av 3-jod-2-propynyl butylkarbamat (IPBC) and 2,2-dibrom-2-cyanoacetamin (DBNPA).

IPBC tillhör kategorin konserveringsmedel/desinfektionsmedel och används som fungicid. Det används inom pappersmassaindustrin för att förhindra slembildning och som konserveringsmedel i kosmetika och färger. DBNPA används i störst utsträckning för att förhindra tillväxt av slembildande mikroorganismer inom pappers- och cellulosaindustrin. Ämnet används också som biocid i kylvattensystem inom industrin.

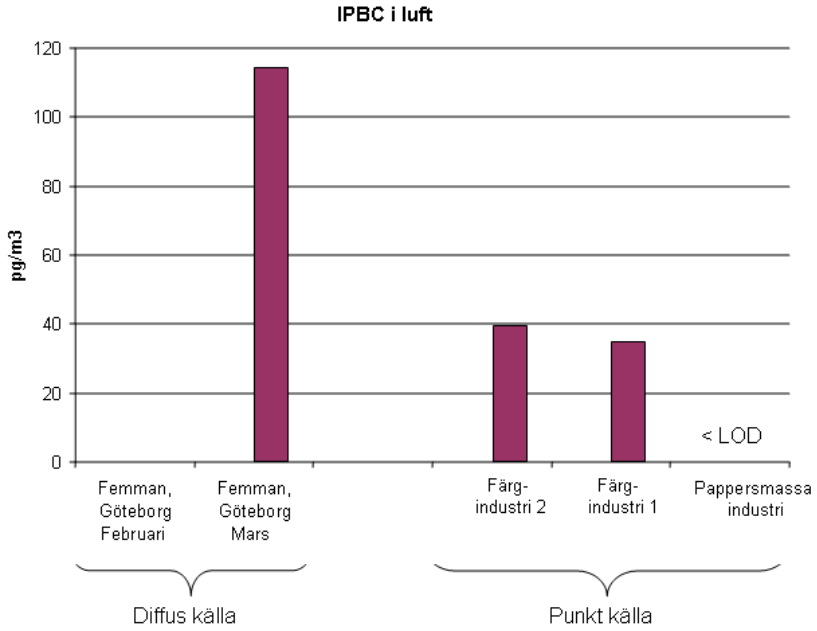
IPBC är måttligt lösligt i vatten och mindre persistent på grund av att föreningen kan genomgå hydrolys. Vattenlösligheten och det låga ångtrycket gör att fördelning till luft är mindre trolig. Spridning och retention av IPBCs i miljön beror på dess fysikaliska och kemiska egenskaper och inte på biotransformationsprocesser.

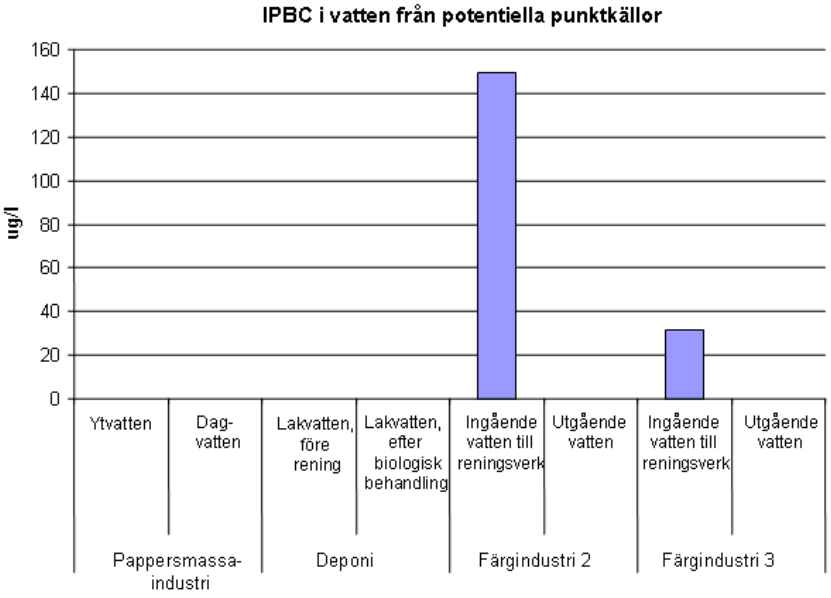
DBNPA har lågt log Kow och lågt ångtryck vilket ger föreningen hög vattenlöslighet. Ämnet har dock kort halveringstid i vatten och bryts snabbt ner genom hydrolys.

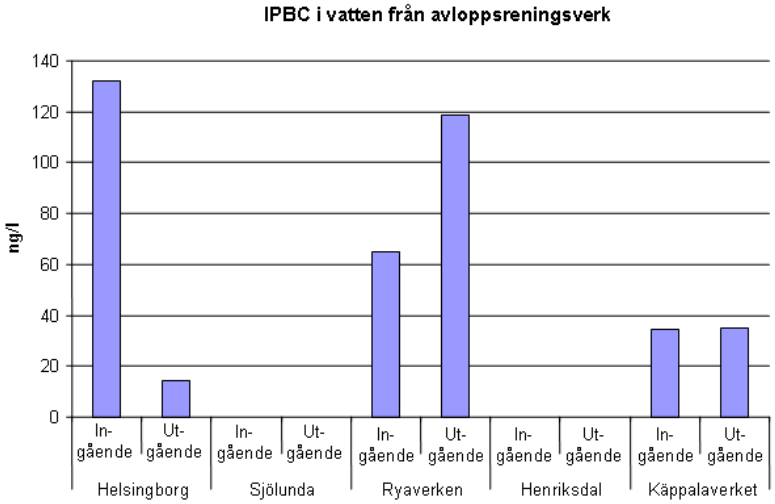
Syftet med föreliggande screening var att utreda förekomsten av IPBC och DBNPA i miljön och i vilken omfattning. En provtagningsstrategi utarbetades utifrån substansernas förutspådda emissionskällor och dess fördelning i miljön. De utvalda provtagningsplatserna representerar punktkällor så som färgindustri och pappersmassaindustri, diffusa källor i urban miljö, avloppsreningsverk samt bakgrundsområden. Proverna bestod av luft, ytvatten, sediment, jord, ingående och utgående avloppsvatten, avloppsslam, dagvatten och dagvattenslam.

IPBC återfanns i luft utanför två färgindustrier samt i centrala Göteborg, se figur IPBC i luft nedan. I ingående vatten till två färgindustriers interna reningsverk återfanns IPBC i höga koncentrationer, se figur IPBC i vatten från potentiella punktkällor. I det utgående vattnet var koncentrationerna betydligt lägre. I tre avloppsreningsverk hittades IPBC i både det utgående och ingående vattnet medan det var under detektionsgränsen i två reningsverk., se figur IPBC i vatten från avloppsreningsverk. IPBC kunde inte detekteras i fasta matriser så som jord, sediment eller slam oberoende om det var nära punkt eller diffus källa, eller i urbant vatten. Prover tagna från platser definierade som backgrundområden innehöll inte heller IPBC.

Resultaten visar att IPBC hittas i miljön där det används och skulle kunna ha en spridning vidare ut i miljön via luft och avloppsvatten. IPBC hittas dock inte i ytvatten från urban miljö.


IPBC i luft
pg/m3
120
100
80
60
40
20
0
< LOD
Femman, Göteborg Februari
Femman, Göteborg Mars
Färg-industri 2
Färg-industri 1
Pappersmassa industri
Diffus källa
Punkt källa


IPBC i vatten från potentiella punktkällor
ug/l
160
140
120
100
80
60
40
20
0
Ytvatten
Dag-vatten
Lakvatten, före rening
Lakvatten, efter biologisk behandling
Ingående vatten till reningsverk
Utgående vatten
Ingående vatten till reningsverk
Utgående vatten
Pappersmassa-industri
Deponi
Färgindustri 2
Färgindustri 3



Halterna av DBNPA var under detektionsgränsen i samtliga prover vilket till största sannolikhet beror på den snabba nedbrytningen av föreningen.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL Swedish Environmental Research Institute has during 2008/2009 performed a "Screening Study" of 3-Iodo-2-propynyl butyl carbamate (IPBC) and 2,2-dibromo-2-cyanoacetamine (DBNPA).

IPBC belongs to the category preservatives/disinfectants and is used as a fungicide. It is used in the paper and pulp industry to prevent the formation of slime and as a preservative in cosmetics, paints, coatings etc. DBNPA is mostly used to reduce the occurrence of slime forming microorganisms with in the paper and cellulose industry. It is also used a biocide in cooling systems.

IPBC is moderately soluble and not persistent in water, hydrolysis is expected to be the main route of dissipation. The water solubility and low vapor pressure of IPBC make the compound not likely to partition to the atmosphere or undergo long range transport or deposition. The fate of IPBC in receiving waters is dependent on physicochemical processes rather than biotransformation.

DBNPA has low vapor pressure and high water solubility which make the compound to be retained mainly in the water phase. However, DBNPA has a short half-life and is rapidly degraded in water by hydrolysis.

The overall objectives of this screening study were to determine the concentrations of IPBC and DBNPA in the Swedish environment and to assess the possibility of current emissions. A sampling strategy was developed in order to determine concentrations of these compounds in different matrices. Selected sampling sites represent point sources in urban environments, diffuse sources and background areas.

IPBC was found in air at two paint companies representing point sources and in the centre of Gothenburg, representing an urban diffuse source. In water, IPBC was found at high levels in the influent water to treatment plants at two paint companies and in both influent and effluent water from three STPs. It was not found in background areas or in urban surface water, storm water sediment, STP sludge or storm water sludge.

The results indicate that if IPBC is being used, and that there is a possibility for the compound to be distributed to the environment since in can be detected in air and influent and effluent water from treatment plants at paint industries and in STP waters. However, IPBC does not seem to reach urban or background areas.

DBNPA was not found in any of the samples. This is probably due to the rapid degradation of the compound.

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1 Introduction

As an assignment from the Swedish Environmental Protection Agency, a screening study has been performed by IVL during 2008/2009. This screening includes biocides, unintentionally produced substances and fuel additives. These substances/substance groups are emitted and distributed in the environment via a variety of sources, e.g. different point sources and/or diffusive sources. Table 1 shows the major reason for their concern as well as the number of the report where individual results are presented.

Table 1. Substances / substance groups included in the screening.

Substance / Substance group		Banned/ restricted	HPV[a]	Indications of toxicity	B/P[b]	Sub-report #
Biocides	**3-Iodo-2-propynyl butyl carbamate (IPBC) 2,2-Dibromo-2-cyanoacetamide (DBNPA)**			**x**		**1**
	Glutaraldehyde		x	x		2
	Difenacoum	x		x	x	3
Unintentionally produced substances	Nitro-PAH 3-Nitrobezantron Oxy-PAH Heterocyclics Brominated dioxins and aromatics			x	x	4
Fuel additives	Methyl *tert*-butyl ether (MTBE) Ethyl *tert*-butyl ether (ETBE)		x	x	x	5

[a] High Production Volume
[b] Bioaccumulation/Persistence

The overall objectives of the screening studies are 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.

Due to the variety in emission sources and use as well as differences in chemical properties, the screening has been carried out in five subprojects. This sub-report concerns the screening of **IPBC and DBNPA**. Results for the other chemicals are presented in subreport 2, 3, 4 and 5.

2 Chemical properties, fate and toxicity

Figure 1 shows the chemical structure of IPBC and DBNPA and Table 2 shows the names, CAS numbers and some chemical and physical data of the compounds. The chemical and physical data of IPBC and DBNPA are gathered from ChemIDplus.

IPBC DBNPA

Figure 1. Chemical structure of 3-Iodo-2-propynyl bytylcarbamate (IPBC) and 2,2-Dibromo-2-cyanoacetamide (DBNPA).

Table 2. Chemical and physical data of 3-Iodo-2-propynylbytylcarbamate (IPBC) and 2,2-Dibromo-2-cyanoacetamide (DBNPA).

Name	CAS#	MW (g/mol)	Melting Point (˚C)	Log Kow	Water Solubility (mg/L)	Vapor Pressure
3-Iodo-2-propynyl bytylcarbamate (IPBC)	55406-53-6	281	64-66.5	2,8	156 at 20 ˚C	9.96E-8 Atm at 20 ˚C
2,2-Dibromo-2-cyanoacetamide (DBNPA)	10222-01-2	240	124.5	0.82	15 000 at 20 ˚C	9.00E-4 mm Hg at 20 ˚C

2.1 Properties and fate

IPBC belongs to the category preservatives/disinfectants and is used as a fungicide. It is also used in the paper and pulp industry to prevent the formation of slime and as a preservative in cosmetics, paints, coatings etc. DBNPA is mostly used to reduce the occurrence of slime forming micro-organisms within the paper and cellulose industry. It is also used as a biocide in cooling systems.

IPBC is moderately soluble in water, and is not likely to adsorb to suspended solids or sediment, it is more likely to remain in the dissolved phase (Juergensen et al. 2000). It is not persistent in the water column; hydrolysis is expected to be the main route of dissipation. IPBC is not expected to bioaccumulate and has a bioconcentration factor of <4.5 (Juergensen et al. 2000). The water solubility and low vapor pressure of IPBC makes the compound not likely to partition to the atmosphere or undergo long range transport or deposition. The fate of IPBC in receiving waters is dependent on physicochemical processes rather than biotransformation. The persistence of IBPC in natural water was estimated to be less than seven days (Juergensen et al. 2000).

For DBNPA, the low vapor pressure and high water solubility should make the compound to retain mainly in the water phase. Therefore there is a possibility for the compound to be distributed to the environment and water recipient and less probably be distributed to soils and sediments. However, the short half life in water due to hydrolysis is probably the main factor that determines the residence time in water and the distribution of it from the emission source. The half –life of DBNPA in water has been set to a mean of 0.5 h when used in model calculations for risk assessment (Klaine et al. 1996).

In water DBNPA is rapidly hydrolysed to dibromoacetonitrile (Blanchard et al. 1987). The presence of organic material in the water leads to a second pathway where monobromonitrilopropionamide is being formed.

2.2 Toxicity

IPBC is listed as one of the most commonly used industrial antifungal agents according to "World Guide to Industrial Biocides", as described by Nakashima et al. 2000. It has been detected in metalworking fluids (Henricks-Eckerman et al. 2008) and a few cases of contact allergy to it have been reported (Bryld et al. 1997, Majoie et al. 2000).

IPBC is potentially toxic to nontarget organisms in the aquatic environment arising from accidental release or leaching of IPBC-containing formulations. IPBC has been reported to affect fathead minnows at levels of 0.019 mg/L and *Daphnia magna* at levels of 0.07 mg/L (Juergensen et al. 2000). More acute and chronic toxicity for fresh water fish and invertebrates are reviewed and summarized in Juergensen et al 2000. Information regarding the environmental toxicology, chemistry and fate of IPBC in the Canadian environment has been gathered and used to develop an interim Canadian guideline for the protection of fresh water life for IPBC and al level of 1.9 μg/L is recommended (Juergensen et al. 2000).

Due to a short half life of DBNPA in aquatic environments, it has been concluded that it does not present a significant risk to aquatic ecosystems from possible exposure from industrial cooling systems where DBNPA is being used (Klaine et al. 1996).

A 48-h EC50 of 0.96 mg/L for *Daphnia magna* for DBNPA was referred to in Rigol et al. 2004 where a bioluminicence inhibition test of the bacteria *Vibrio fisheri* gave a EC50 of 0.50 mg/L for DBNPA (Rigol et al. 2004).

3 Production, use and emission

IPBC is imported to Sweden as a fungicide and is used in the production of paint and lacquer and in work up fluids in the metal industry as a preservative (www.kemi.se). It occurs in 512 preparations in Sweden in 2007 and 93 tonnes were used in the same year (SPIN 2009). IPBC is one of the most commonly present allergens in shampoos in the U.S (Zirwas and Moennich 2009).

IPBC may enter the environment through leachate or storm water runoff from freshly treated lumber (Juergensen et al. 2000).

The main use of DBNPA in the U.S. is as a biocide in cooling systems, which also represents the greatest potential for environmental exposure. DBNPA has been manufactured and sold by The Dow Chemical Company since 1973, the greatest producer of the compound in the U.S. In Sweden, DBNPA occurs in 41 preparations and 149 tonnes was used per year in 2007 (SPIN 2009). It is used as a biocide in the manufacture of pulp, paper and paper products in Sweden.

4 Previous measurements in the environment

The information of the detection of IPBC in the environment is very limited. IPBC is thought to have moderate potential for movement through soil, groundwater contamination may be possible. In contrast, it has been suggested that IPBC should not threaten groundwater because it appears to rapidly degrade in both aquatic and terrestrial environments (Juergensen et al. 2000). However, IPBC was detected in sediments close to lumber mills using IPBC formulations in the range of 0.19-0.49 μg/g dry weight (Juergensen et al. 2000). With a log K_{ow} of 2.81 and a bioconcentration factor of < 4.5, IBPC has a low potential for accumulation and it has not been found in biota.

DBNPA has been analysed in waters from a recycling paper mill that uses biocides for the improvement of the water quality (Rigol et al. 2002, Rigol et al. 2004). The concentration of DBNPA in the process water was 59 μg/L and was 4.2 μg/L in the outlet primary treatment water (Rigol et al. 2004).

5 Sampling strategy and study sites

5.1 Screening program

A sampling strategy was developed in order to determine concentrations of IPBC and DBNPA in different matrices in the Swedish environment.

The sampling programme was based on the identification of possible sources due to the use and the possibility for the compounds to distribute in the environment. The sampling programme is summarized in Table 3 for IPBC and in Table 4 for DBNPA. Details on the samples can be found in Table A1 and A3 in the Appendix.

For IPBC air samples were collected at background areas and urban areas. Samples were also collected at three different paint production industries, i.e. possible point sources due to the use of the compound. Different types of water samples (influent, effluent, leachate and storm water) as well as sediment were also sampled at the point sources. The point sources consist of samples from the paper and pulp industry, one landfill and paint companies. Samples from diffuse sources were collected in the cities of Gothenburg and Stockholm were air, surface water, soil, sediment and storm water samples were collected. From Sewage treatment plants (STP), both influent and effluent water were sampled as well as sludge.

DBNPA has a similar sampling programme as IPBC. Due to the physical and chemical properties, the most relevant matrices for DBNPA are water (surface water, process water and STP influent and effluent water). The short half life of the compound makes point sources where DBNPA is being used of great interest. Several different water samples have been collected at a paper and pulp industry.

In order to determine background levels, samples of soil, sediment, surface water and fish were analysed from three background lakes, classified as reference lakes by the Swedish Museum of National History.

Due to the low log Kow of the compounds and especially DBNPA, i.e. they will not bioaccumulate, biota samples were not considered in the program.

Table 3. Sampling program for IPBC

Site	Air	Surface water	Sedi-ment	Soil	Storm water	Storm water sludge	Industry water	STP Water (in)	STP water (out)	STP sludge	Leach-ate	Total
Background												
Råö	2											2
Lakes		3	2									2
Diffuse sources												
Urban area	2	3	3	2	5	3						18
STP								5	5	5		15
Point sources												
Paper & pulp industry	1	1		2	1							5
Paint production industry	2						4					6
Landfill											2	2
Total	7	7	5	4	6	3	4	5	5	5	2	53

Table 4. Sampling program for DBNPA

Site	Air	Surface water	Sedi-ment	Soil	Storm water	Storm water sludge	Industry water	STP Water (in)	STP water (out)	STP sludge	Leach-ate	Total
Background												
Råö	2											2
Lakes		3	2									5
Diffuse sources												
Urban area	2	3	3	2	5	3						18
STP								5	5	5		15
Point sources												
Paper & pulp industry	1	1			1		2					7
Landfill											2	2
Total	5	7	5	4	6	3	2	5	5	5	2	49

6 Methods

6.1 Sampling

The staff at the different sewage treatment plants collected de-watered **sludg**e samples from the anaerobic chambers. The sludge was transferred into glass jars and stored in a freezer (-20 ºC) until analysed. **Influent** and **effluent** waters were sampled in 1 or 2 L glass bottles.

Surface **sediment** (0-2 cm) samples were collected by means of a Kajak sampler. The sediment was transferred into glass jars and stored in a freezer (-20 ºC) until analysed. One sediment sample from the background lake Tärnan was provided from the specimen bank at the Swedish Museum of Natural History.

Surface water samples from background lakes and from the city of Stockholm were sampled in glass bottles and the pH was adjusted to pH 2 with H_3PO_4 and stored in at 6 ºC.

The upper 2-3 cm of surface **soil** was collected in glass jars.

Storm water samples were provided by the Swedish Road Administration (Vägverket) and "Gatukontoret" in Göteborg.

Air samples were collected using a low volume air sampler (LVS) with a flow of approximately 1 m^3/h. The air was passed through a glass fiber filter (MG160, Munktell) where the particles were collected and then through a glass column packed with the adsorbents XAD-2 (Amberlite) and polyurethane foam (PUF). Sampling duration was one week at the point sources and two weeks at the background station for IPBC. For DBNPA, the sampling duration was 2-3 days at the background station and 1-2 days at the point sources. Prior to sampling, glass fiber filters were heated to 400 ºC, and the adsorbents columns were cleaned by Soxhlet extraction with acetone. After sampling, the filter and columns were wrapped in aluminum foil and send to the laboratory, where they were stored in a freezer (-20 ºC) until analysed. Additional filters and columns used as field blanks were sent back to the laboratory unexposed.

All glass equipment used was muffled (400 ºC) before use.

6.2 Sample preparation

6.2.1 Solid samples

IPBC and DBNPA were extracted from the solid samples simultaneously. Sludge (0.5 g), storm water sludge (0.5 g), sediment (1.5-2 g) and soil (1.5-2 g) were ground with Na_2SO_4 and extracted twice with 30 ml acetone by one hour rotation. The volumes were reduced and the solvent was exchanged to methanol (5 ml) before HPLC-MS/MS analysis.

6.2.2 Water samples

IPBC and DBNPA were extracted from the water samples simultaneously. An Oasis HLB SPE column (200 mg, Waters) was activated with methanol and acidic water before the water was extracted. The trapped analytes were then eluted with 5 ml acetone and the solvent was exchanged to methanol. The final sample volume was 1 ml.

Volumes used: surface water: 400 ml, storm water 100 mL, influent water from sewage treatment plant: 100 ml, effluent water from sewage treatment plant: 200 ml, and leachate water 100 mL.

6.2.3 Air samples

IPBC and DBNPA were extracted from the adsorbent using 100 ml of methanol. The solvent volume was reduced to 2 ml by a rotary evaporator.

6.3 Instrumentation

The extracts were analyzed applying high performance liquid chromatography using a Prominence UFLC system (Shimadzu) with two pumps LC 20AD, degasser DGU-20A5, auto sampler SIL-20ACHT and column oven CTO-20AC. The analytical column was a Thermo HyPurity C8 50 mm x 3 mm, particle size 5 µm (Dalco Chromtech). The column temperature was 30 ºC. For analysis, 10 µl sample extract in methanol were injected.

IPBC: Mobile phase A was 2 mM ammonium acetate in water. Solvent B was methanol, adopted from Henriks-Eckerman et al. (2008). The flow rate of the mobile phase was 0.4 ml/min. A gradient elution was performed: 0-2 min 30% B, 2-10 min linear increase to 95% B, 10-14 min isocratic 95% B, 14-16 min linear decrease to 30% B. Equilibration time. 5 min.

DBNPA: Mobile phase A was 0.1% formic acid in water. Solvent B was methanol. The flow rate of the mobile phase was 0.4 ml/min. A gradient elution was performed: 0-3 min 10% B, 3-6 min linear increase to 95% B, 6-10 min isocratic 95% B, 10-12 min linear decrease to 10% B. Equilibration time. 7 min.

The effluent was directed to an API 4000 triple quadrupole mass spectrometer (Applied Biosystems).

For the analysis of IPBC electrospray ionisation (ESI) in negative mode was used. Two MRM transitions according to Table 5 was recorded. Calibration was done using standard curves based on areas vs. known concentrations of the actual compound. The sample extracts were adjusted to known volumes. No internal standards were used since it was not possible to find representative compounds.

Table 5. Instrumental parameters for determination of IPBC.

	Precursor ion m/z	Product ion m/z	Declustering potential, V	Collosion energy, V
MRM1	282	165	52	27
MRM2	165	127	100	50

For DBNPA it was not possible to obtain stable MRM signals. Probably the compound is thermally degraded in the ion source. Instead the ions m/e 79 and 81 (bromine) were selected by both quadrupoles in the instrument .

6.4 Quality control

6.4.1 IPBC

Detection was done using two independent MRM transitions. MRM 282/165 was used for quantification and MRM 165/127 was used as qualifier. Also, the retention time should match the authentic standard compound within ± 0.1 min.

For each matrix, two solvent method blanks were prepared in parallel with the samples to assess possible interferences and contamination from the background.

The background contamination in the blank samples was subtracted from the measured sample values. Limit of detection (LOD) was defined as three times the standard deviation of the noise of the blank water samples and adjusted for the different volumes used In the solid matrixes LOD was calculated as ten times the blank level and for the air samples as three times the level in the field blank.

6.4.2 DBNPA

The relationship for the two bromide isotopes 79 and 81 is 1:1. A standard curve was prepared and showed a linear relationship between 1000 ng/ml and 25 ng/ml. In this range the relationship between the two isotopes are 1:1 but divides from this at concentrations lower than 25 ng/ml. Limit of detection (LOD) was calculated from this value, i.e. 25 ng/ml was multiplied with the final volumes for the sample extracts and then divided with the sample amount.. It was not possible to calculate a LOD value from noise in the solvent blank samples.

Samples with a strong signal for m/z 81 were also analysed on GC-MS/MS in the full scan mode to compare the spectra with an authentic standard.

For each matrix, solvent method blanks were prepared in parallel with the samples to assess possible interferences and contamination from the background.

7 Results and discussion

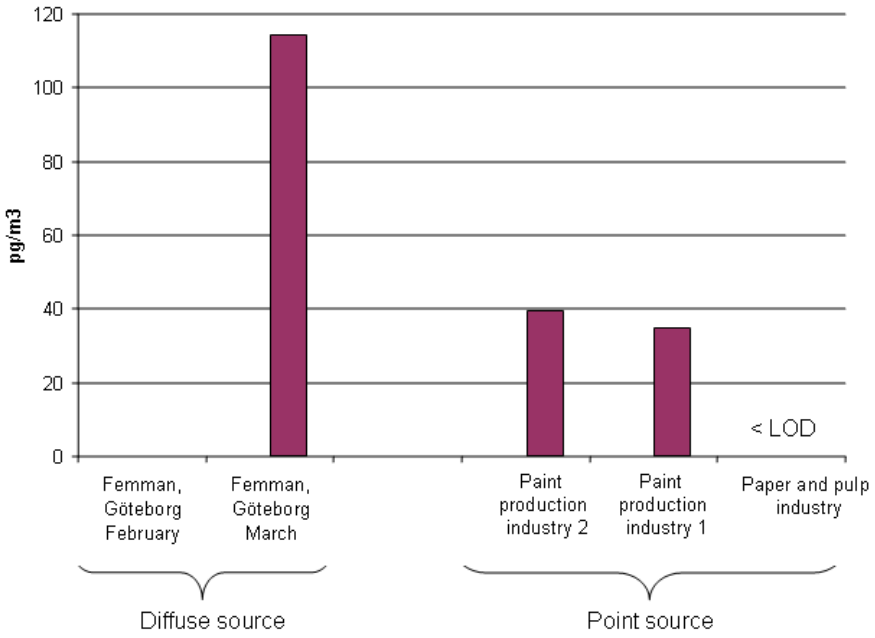
7.1 IBPC

IPBC could be found in one air sample representing an urban diffuse source and in two air samples from potential point sources. In water, IPBC was found in several samples at both point sources and diffuse STP sources. It was not found in background areas or in urban surface water, storm water, soil and sediment, STP sludge or storm water sludge. The results from in air and water are presented in figures below. All results and LOD can be found in Table A2 in the Appendix.

7.1.1 Air

IPBC was found in air from both diffuse and point sources, see Figure 2. Femman is a mall in the centre of Gothenburg. The air sampler was up in two periods, following each other directly. At the first sampling occasion, in the end of February, the concentration was below LOD and at the next occasion in the beginning of March, the concentration was 110 pg/m^3. This may be due to that work was being performed at Femman were products were used that contained IPBC. This also shows that the detection of IPBC in the environment may be a coincidence due to the sampling occasion.

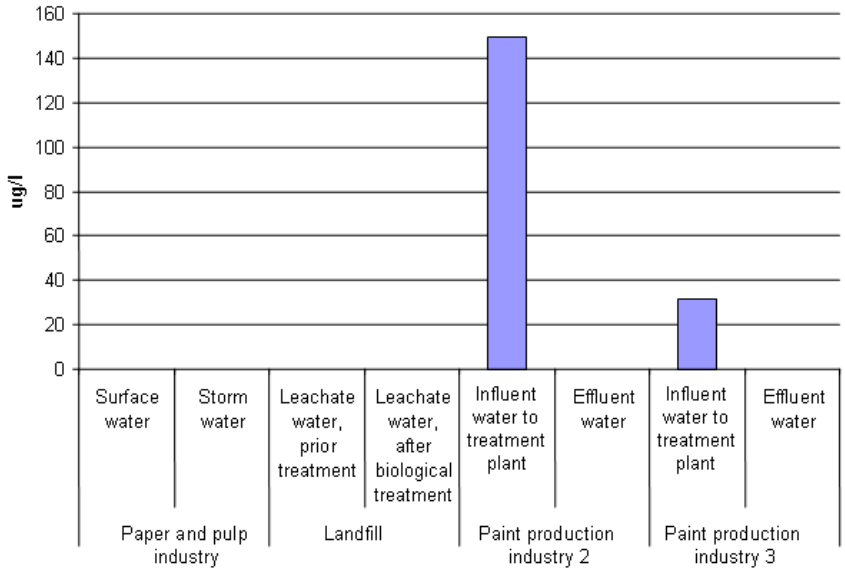
IPBC is a component in paint and IPBC was found at in the air both Paint production industry 1 and 2. IPBC is also used in the paper industry but the concentration where below LOD in the air sample from the paper and pulp industry in this study. It could be due to that IPBC is not being used at this company or that it was not detectable at the sampling occasion.



Figur 2. Concentrations of IPBC (pg/m³) in air from a diffuse urban area and from point sources, i.e. paint industry and paper and pulp industry.

7.1.2 Water, Point sources

IPBC was detected at high concentrations, 150 and 32 ug/l respectively, in the influent waters to the treatment plants at two paint industries, see Figure 3. The effluent waters from these companies also contained IPBC but at much lower levels, 0.032 and 0.22 ug/l. IBPC was not detected in surface or storm water at the other potential point source, a land fill. The land fill, contained 0.035 ug IPBC/l in the water prior to treatment.

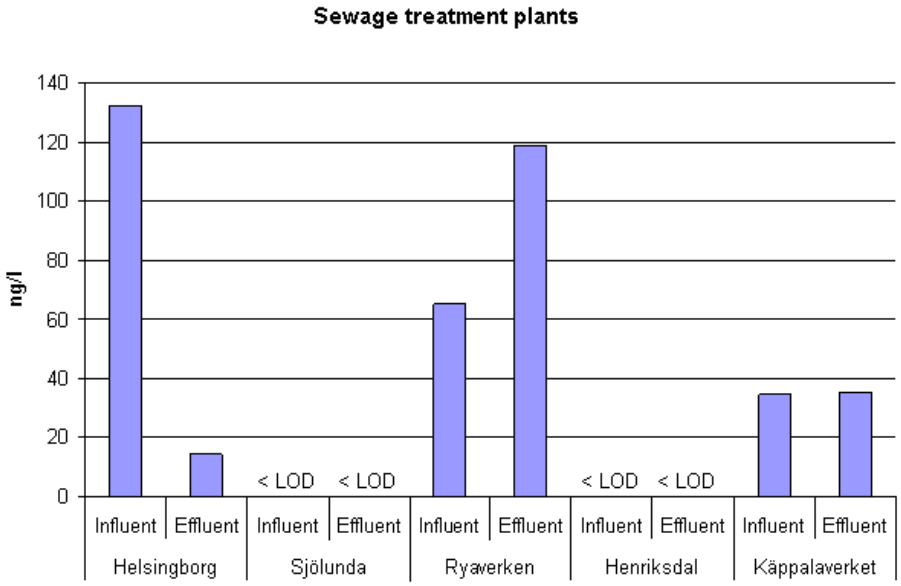


Figur 3. IPBC concentrations (ug/l) in influent and effluent water at treatment plants at paint industries, paper and pulp industry and from a landfill (recycling company).

7.1.3 Water, Diffuse sources

IPBC was found in both influent and effluent waters at three STPs, Helsingborg, Ryaverket and Käppalaverket, see Figure 4. Only at Helsingborg there was a trend with lower concentrations in the effluent water compared to the influent water. At Sjölunda and Henriksdal, the concentrations were below LOD. The effluent water from Paint production industry 3 is connected to Sjölunda and with respect to dilution and hydrolysis, it seem reasonable that the concentrations at Sjölunda is below LOD. However, IPBC was found in similar or higher levels in the effluent water compared to the influent water at Käppalaverket and Ryaverket. Therefore it is a possibility that IPBC may enter the water after treatment. Also, the detection in the effluent water enhances the risk for IPBC to reach the environment.

The Canadian guideline for the protection of fresh water life is 1.9 ug/L (Jueregensen et al 2000) and the effluent water at the STPs where IPBC could be detected is at least 14 times lower.



Figur 4. Concentrations of IPBC (ug/l) in STP influent and effluent water.

7.2 DBNPA

DBNPA was not be found in any of the samples. In the environment DBNPA is rapidly degraded primarily through hydrolysis but it may also be degraded during the analytical procedure.

All samples contained a peak, often with an asymmetric shape, at the expected retention time. However, the relationship between the bromide isotopes 79 and 81 was far from 1:1 in all samples. Due to this, the peaks were considered NOT to be DBNPA. The calibration curve showed that sample extracts must contain levels above 25 ng/ml to ensure the identity of the compound. When MRM is used with in mass spectrometry it is desirable to use an ion pair with masses from the parent compound and a fragment that is specific for the compound. This was not possible to do for DBNPA since it is too instable to pass the analytical instrument with out being degraded, therefore only m/z 79 and m/z 81 could be used. The LODs for the different matrices, calculated from 25 ng/ml as described in section 6.4.2, are summarized in Table 6. Details for respective sample can be found in Table A3 in the Appendix.

Table 6. Limit of detection (LOD) for the different matrices analysed in the study.

Matrix	LOD	Matrix	LOD
Surface water	300 ng/L	Air	< 1 ng/m^3
Storm water	1250 ng/L	Sediment	< 60 ng/g f.v.
Leachate water	1250 ng/L	Soil	< 60 ng/g f.v.
Influent water	1250 ng/L	Sludge	< 250 ng/g f.v.
Effluent water	625 ng/L		

8 Conclusions

- IPBC was found in air in urban areas, in air close to point sources and in waste water at industries where it is being used.
- IPBC occured in both influent and effluent water at STPs. The occurrence in effluent water indicated that it has a potential to reach the environment.
- IPBC was not found either in background or urban surface water, sediment and soil.
- DBNPA was not found in any of the samples. This is probably due to the rapid degradation of the compound.

9 Acknowledgement

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Annika Potter and Katarina Hansson at IVL in Gothenburg are acknowledged for their assistants in collecting and providing samples.

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Table A1. Sample information from the screening programme for IPBC.

Sample ID	Category	Site	Sampling date	Matrix	DW (%)	Notes
7806	Background	Råö	2009-02-27 - 2009-03-10	Air		
7847	Background	Råö	2009-03-30 - 2009-04-15	Air		
7674	Background	Gårdsjön	2008-11-20	Sediment	4	
7708	Background	Tärnan	2008-09-23	Sediment	10	
7679	Background	Gårdsjön	2008-11-20	Surface water		
7615	Background	Tärnan	2008-11-30	Surface water		
7616	Background	Largen	2008-11-31	Surface water		
7794	Point source	Paper and pulp industry	2009-03-06 - 2009-03-13	Air		
7790	Point source	Paint production 1	2009-02-26 - 2009-03-05	Air		
7795	Point source	Paint production 2	2009-02-25 - 2009-03-04	Air		
7811	Point source	Paper and pulp industry	2009-03-05	Soil	72	
7812	Point source	Paper and pulp industry	2009-03-05	Soil	72	
7831	Point source	Landfill	2009-04-22	Leachate water		Prior treatment
7832	Point source	Landfill	2009-04-22	Leachate water		After biological treatment
7813	Point source	Paper and pulp industry	2009-03-05	Surface water		
7789	Point source	Paper and pulp industry	2009-03-04	Storm water		
7777	Point source	Paint production 3	2009-02-23	Influent water		Prior chemical treatment
7837	Point source	Paint production 2	2009-04-21	Influent water		Prior treatment
7838	Point source	Paint production 2	2009-04-21	Effluent water		After treatment
7778	Point source	Paint production 3	2009-02-23	Effluent water		After chemical treatment
7810	Diffuse, urban	Göteborg, Femman	2009-02-24 - 2009-03-02	Air		
7807	Diffuse, urban	Göteborg, Femman	2009-03-04 - 2009-03-12	Air		
7669	Diffuse, urban	Stockholm, Vårbergstoppen	2009-02-13	Soil	28	
7670	Diffuse, urban	Stockholm, Årstafältet	2009-02-16	Soil	68	
7585	Diffuse, urban	Stockholm, St Essingen	2008-11-08	Sediment	18	
7583	Diffuse, urban	Stockholm, Årstaviken	2008-11-08	Sediment	16	
7584	Diffuse, urban	Stockholm, Riddarfjärden	2008-11-08	Sediment	16	
7582	Diffuse, urban	Stockholm, St Essingen	2008-11-08	Surface water		
7578	Diffuse, urban	Stockholm, Årstaviken	2008-11-10	Surface water		

Sample ID	Category	Site	Sampling date	Matrix	DW (%)	Notes
7581	Diffuse, urban	Stockholm, Riddarfjärden	2008-11-08	Surface water		
7845	Diffuse, urban	Stockholm, Årstafältet	2009-04-27	Storm water		
7846	Diffuse, urban	Stockholm, Huddinge	2009-04-27	Storm water		
7771	Diffuse, urban	Göteborg, Odingsplatsen	2009-02-23	Storm water		
7773	Diffuse, urban	Göteborg, Gårda	2009-02-23	Storm water		
7775	Diffuse, urban	Göteborg, Korsvägen	2009-02-23	Storm water		
7772	Diffuse, urban	Göteborg, Odingsplatsen	2009-02-23	Storm water sludge	22	
7774	Diffuse, urban	Göteborg, Gårda	2009-02-23	Storm water sludge	19	
7776	Diffuse, urban	Göteborg, Korsvägen	2009-02-23	Storm water sludge	41	
7766	Diffuse, STP	Henriksdal	2009-01-30	Sludge	27	
7726	Diffuse, STP	Käppalaverket	2008-12-15	Sludge	17	
7760	Diffuse, STP	Ryaverken	2009-01-29	Sludge	32	
7841	Diffuse, STP	Helsingborg	2009-04-20	Sludge	25	
7782	Diffuse, STP	Sjölunda	2009-02-23	Sludge	23	
7722	Diffuse, STP	Henriksdal	2008-12-16	Influent water		
7724	Diffuse, STP	Käppalaverket	2008-12-16	Influent water		
7839	Diffuse, STP	Helsingborg	2009-04-21	Influent water		
7779	Diffuse, STP	Sjölunda	2009-02-23	Influent water		
7761	Diffuse, STP	Ryaverken	2009-01-29	Influent water		
7723	Diffuse, STP	Henriksdal	2008-12-16	Effluent water		
7725	Diffuse, STP	Käppalaverket	2008-12-16	Effluent water		
7840	Diffuse, STP	Helsingborg	2009-04-21	Effluent water		
7784	Diffuse, STP	Sjölunda	2009-02-23	Effluent water		
7762	Diffuse, STP	Ryaverken	2009-01-29	Effluent water		

Table A2. Concentration of IPBC in samples from the screening programme.

Sample ID	Category	Site	Matrix	Sampling date	Unit	Conc
7806	Background	Råö	Air	2009-02-27 - 2009-03-10	pg/m^3	< 20
7847	Background	Råö	Air	2009-03-30 - 2009-04-15	pg/m^3	< 20
7674	Background	Gårdsjön	Sediment	2008-11-20	ng/g f.v.	< 0.3
7708	Background	Tärnan	Sediment	2008-09-23	ng/g f.v.	< 0.3
7679	Background	Gårdsjön	Surface water	2008-11-20	ng/l	< 5
7615	Background	Tärnan	Surface water	2008-11-30	ng/l	< 5
7616	Background	Largen	Surface water	2008-11-31	ng/l	< 5
7794	Point source	Paper and pulp industry	Air	2009-03-06 - 2009-03-13	pg/m3	< 20
7790	Point source	Paint production 1	Air	2009-02-26 - 2009-03-05	pg/m^3	35
7795	Point source	Paint production 2	Air	2009-02-25 - 2009-03-04	pg/m^3	39
7811	Point source	Paper and pulp industry	Soil	2009-03-05	ng/g f.v.	< 0.3
7812	Point source	Paper and pulp industry	Soil	2009-03-05	ng/g f.v.	< 0.3
7831	Point source	Landfill	Leachate water	2009-04-22	ng/l	35
7832	Point source	Landfill	Leachate water	2009-04-22	ng/l	< 10
7813	Point source	Paper and pulp industry	Surface water	2009-03-05	ng/l	< 5
7789	Point source	Paper and pulp industry	Storm water	2009-03-04	ng/l	< 10
7777	Point source	Paint production 3	Influent water	2009-02-23	ng/l	31500
7837	Point source	Paint production 2	Influent water	2009-04-21	ng/l	149000
7838	Point source	Paint production 2	Effluent water	2009-04-21	ng/l	32
7778	Point source	Paint production 3	Effluent water	2009-02-23	ng/l	220
7810	Diffuse, urban	Göteborg, Femman	Air	2009-02-24 - 2009-03-02	pg/m^3	< 20
7807	Diffuse, urban	Göteborg, Femman	Air	2009-03-04 - 2009-03-12	pg/m^3	110
7669	Diffuse, urban	Stockholm, Vårbergstoppen	Soil	2009-02-13	ng/g f.v.	< 0.3
7670	Diffuse, urban	Stockholm, Årstafältet	Soil	2009-02-16	ng/g f.v.	< 0.3
7585	Diffuse, urban	Stockholm, St Essingen	Sediment	2008-11-08	ng/g f.v.	< 0.3
7583	Diffuse, urban	Stockholm, Årstaviken	Sediment	2008-11-08	ng/g f.v.	< 0.3
7584	Diffuse, urban	Stockholm, Riddarfjärden	Sediment	2008-11-08	ng/g f.v.	< 0.3
7582	Diffuse, urban	Stockholm, St Essingen	Surface water	2008-11-08	ng/l	< 2.5
7578	Diffuse, urban	Stockholm, Årstaviken	Surface water	2008-11-10	ng/l	< 2.5
7581	Diffuse, urban	Stockholm, Riddarfjärden	Surface water	2008-11-08	ng/l	< 2.5

Sample ID	Category	Site	Matrix	Sampling date	Unit	Conc
7845	Diffuse, urban	Stockholm, Årstafältet	Storm water	2009-04-27	ng/l	< 10
7846	Diffuse, urban	Stockholm, Huddinge	Storm water	2009-04-27	ng/l	< 10
7771	Diffuse, urban	Göteborg, Odingsplatsen	Storm water	2009-02-23	ng/l	< 10
7773	Diffuse, urban	Göteborg, Gårda	Storm water	2009-02-23	ng/l	< 10
7775	Diffuse, urban	Göteborg, Korsvägen	Storm water	2009-02-23	ng/l	< 10
7772	Diffuse, urban	Göteborg, Odingsplatsen	Storm water sludge	2009-02-23	ng/g f.v.	< 1
7774	Diffuse, urban	Göteborg, Gårda	Storm water sludge	2009-02-23	ng/g f.v.	< 1
7776	Diffuse, urban	Göteborg, Korsvägen	Storm water sludge	2009-02-23	ng/g f.v.	< 1
7766	Diffuse, STP	Henriksdal	Sludge	2009-01-30	ng/g f.v.	< 1
7726	Diffuse, STP	Käppalaverket	Sludge	2008-12-15	ng/g f.v.	< 1
7760	Diffuse, STP	Ryaverken	Sludge	2009-01-29	ng/g f.v.	< 1
7841	Diffuse, STP	Helsingborg	Sludge	2009-04-20	ng/g f.v.	< 1
7782	Diffuse, STP	Sjölunda	Sludge	2009-02-23	ng/g f.v.	< 1
7722	Diffuse, STP	Henriksdal	Influent water	2008-12-16	ng/l	< 10
7724	Diffuse, STP	Käppalaverket	Influent water	2008-12-16	ng/l	34
7839	Diffuse, STP	Helsingborg	Influent water	2009-04-21	ng/l	130
7779	Diffuse, STP	Sjölunda	Influent water	2009-02-23	ng/l	< 10
7761	Diffuse, STP	Ryaverken	Influent water	2009-01-29	ng/l	65
7723	Diffuse, STP	Henriksdal	Effluent water	2008-12-16	ng/l	< 5
7725	Diffuse, STP	Käppalaverket	Effluent water	2008-12-16	ng/l	35
7840	Diffuse, STP	Helsingborg	Effluent water	2009-04-21	ng/l	14
7784	Diffuse, STP	Sjölunda	Effluent water	2009-02-23	ng/l	< 5
7762	Diffuse, STP	Ryaverken	Effluent water	2009-01-29	ng/l	120

Table A3. Sample information and results from the screening programme for DBNPA.

Sample ID	Category	Site	Sampling date	Matrix	DW (%)	Notes	Conc
7798	Background	Råö	2009-02-25 - 2009-02-27	Air			< 1 ng/m^3
7814	Background	Råö	2009-03-27 - 2009-03-30	Air			< 1 ng/m^{3}l
7674	Background	Gårdsjön	2008-11-20	Sediment	4		< 60 ng/g f.v.
7708	Background	Tärnan	2008-09-23	Sediment	10		< 60 ng/g f.v.
7679	Background	Gårdsjön	2008-11-20	Surface water			< 300 ng/l
7615	Background	Tärnan	2008-11-30	Surface water			< 300 ng/l
7616	Background	Largen	2008-11-31	Surface water			< 300 ng/l
7797	Point source	Paper and pulp industry	2009-03-05 - 2009-03-06	Air			< 1 ng/m^3
7811	Point source	Paper and pulp industry	2009-03-05	Soil	72		< 60 ng/g f.v.
7812	Point source	Paper and pulp industry	2009-03-05	Soil	72		< 60 ng/g f.v.
7831	Point source	Landfill	2009-04-22	Leachate water			< 1250 ng/l
7832	Point source	Landfill	2009-04-22	Leachate water			< 1250 ng/l
7813	Point source	Paper and pulp industry	2009-03-05	Surface water			< 300 ng/l
7789	Point source	Paper and pulp industry	2009-03-04	Storm water			< 1250 ng/l
7787	Point source	Paper and pulp industry	2009-03-03	Influent water			< 1250 ng/l
7788	Point source	Paper and pulp industry	2009-03-03	Effluent water		After biological treatment	< 625 ng/l
7809	Diffuse, urban	Göteborg, Femman	2009-02-23 - 2009-02-24	Air			< 1 ng/m^3
7796	Diffuse, urban	Göetborg, Femman	2009-03-02 - 2009-03-04	Air			< 1 ng/m^3
7669	Diffuse, urban	Stockholm, Vårbergstoppen	2009-02-13	Soil	28		< 60 ng/g f.v.
7670	Diffuse, urban	Stockholm, Årstafältet	2009-02-16	Soil	68		< 60 ng/g f.v.
7585	Diffuse, urban	Stockholm, St. Essingen	2008-11-08	Sediment	18		< 60 ng/g f.v.
7583	Diffuse, urban	Stockholm, Årstaviken	2008-11-08	Sediment	16		< 60 ng/g f.v.
7584	Diffuse, urban	Stockholm, Riddarfjärden	2008-11-08	Sediment	16		< 60 ng/g f.v.
7582	Diffuse, urban	Stockholm, St. Essingen	2008-11-08	Surface water			< 300 ng/l
7578	Diffuse, urban	Stockholm, Årstaviken	2008-11-10	Surface water			< 300 ng/l
7581	Diffuse, urban	Stockholm, Riddarfjärden	2008-11-08	Surface water			< 300 ng/l
7845	Diffuse, urban	Stockholm, Årstafältet	2009-04-27	Storm water			< 1250 ng/l
7846	Diffuse, urban	Stockholm, Huddinge	2009-04-27	Storm water			< 1250 ng/l
7771	Diffuse, urban	Göteborg, Odingsplatsen	2009-02-23	Storm water			< 1250 ng/l

Sample ID	Category	Site	Sampling date	Matrix	DW (%)	Notes	Conc
7773	Diffuse, urban	Göteborg, Gårda	2009-02-23	Storm water			< 1250 ng/l
7775	Diffuse, urban	Göteborg, Korsvägen	2009-02-23	Storm water			< 1250 ng/l
7772	Diffuse, urban	Göteborg, Odingsplatsen	2009-02-23	Storm water sludge	22		< 250 ng/g f.v.
7774	Diffuse, urban	Göteborg, Gårda	2009-02-23	Storm water sludge	19		< 250 ng/g f.v.
7776	Diffuse, urban	Göteborg, Korsvägen	2009-02-23	Storm water sludge	41		< 250 ng/g f.v.
7766	Diffuse, STP	Henriksdal	2009-01-30	Sludge	27		< 250 ng/g f.v.
7726	Diffuse, STP	Käppalaverket	2008-12-15	Sludge	17		< 250 ng/g f.v.
7841	Diffuse, STP	Helsingborg	2009-04-20	Sludge	25		< 250 ng/g f.v.
7782	Diffuse, STP	Sjölunda	2009-02-23	Sludge	23		< 250 ng/g f.v.
7760	Diffuse, STP	Ryaverken	2009-01-29	Sludge	32		< 250 ng/g f.v.
7722	Diffuse, STP	Henriksdals	2008-12-16	Influent water			< 1250 ng/l
7724	Diffuse, STP	Käppalaverket	2008-12-16	Influent water			< 1250 ng/l
7839	Diffuse, STP	Helsingborg	2009-04-21	Influent water			< 1250 ng/l
7779	Diffuse, STP	Sjölunda	2009-02-23	Influent water			< 1250 ng/l
7761	Diffuse, STP	Ryaverken	2009-01-29	Influent water			< 1250 ng/l
7723	Diffuse, STP	Henriksdals	2008-12-16	Effluent water			< 625 ng/l
7725	Diffuse, STP	Käppalaverket	2008-12-16	Effluent water			< 625 ng/l
7840	Diffuse, STP	Helsingborg	2009-04-21	Effluent water			< 625 ng/l
7784	Diffuse, STP	Sjölunda	2009-02-23	Effluent water			< 625 ng/l
7762	Diffuse, STP	Ryaverken	2009-01-29	Effluent water			< 625 ng/l