

Screening of benzothiazoles, benzenediamines, dicyclohexylamine and benzotriazoles

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ChEmitEcs
*Organic Chemicals Emitted
from Technosphere Articles*



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1 Summary

A screening study of benzothiazoles, benzenediamines, dicyclohexylamine, and benzotriazoles has been carried out in the framework of the Swedish Environmental Protection Agency's screening program.

The overall objective of a screening study is to determine the concentrations of the selected substances in a variety of media in the Swedish environment. Additional aims are to assess the possible emission sources and to highlight important transport pathways in the environment.

This screening has been carried out in collaboration with the research program ChEmiTecs "Organic Chemicals Emitted from Technosphere Articles" (www.chemitecs.se, financed by the Swedish Environmental Protection Agency). The aim of ChEmiTecs is to increase the scientific understanding of the magnitude of the problem regarding emissions of organic substances from articles with the objective to support policy development in Sweden and Europe.

The benzothiazoles MBT, CBS, DBS and DBD were found in one or more of the sample matrices. The detection frequencies varied both among the substances and the different media. The distribution pattern was most likely affected both by substance properties, *i.e.* the chemical stability and the tendency of a substance to partition to a certain media, and the use and emission pattern. MBT had the highest detection frequency while the other benzothiazoles were more occasionally found. An important pathway of MBT to the environment is via WWTPs, an indication that the occurrence is due to diffuse emission from *e.g.* consumer products. The occurrence in storm water indicates traffic related emissions. MBT and the other benzothiazoles did mainly occur in the aquatic environment. Air transport seems to be of minor importance.

The benzenediamine DPP was occasionally detected in some of the matrices *e.g.* surface water, storm water and sludge.

DCHA was widespread in the environment and it occurred in all sample types except crops. The findings of DCHA in air and deposition indicate that this substance is emitted to air and that atmospheric transport is an important pathway in the environment. The occurrence in storm water as well as in soil indicates that traffic related emissions are important. DCHA was however not found in crops collected in the vicinity to busy roads. Another important pathway for DCHA to the environment is via WWTPs, an indication that the occurrence is due to diffuse emission from *e.g.* consumer products.

There is a widespread occurrence of benzotriazoles in the environment both at background and urban areas. The substances occurred in all the included environmental matrices, air, deposition, surface water, sediment, soil and biota.

The results also showed that diffuse spreading through WWTPs, landfills and storm water may be important for the occurrence in the environment. This indicates that these substances are distributed via use of products. UVP is the benzotriazole with the highest usage volume followed by UV 328 and UV327. These substances were also most often found in the highest concentrations.

In a brief risk assessment for the aquatic pelagic ecosystems no major risks were identified, *i.e.* concentrations were generally below the PNEC in surface water and effluents if dilution was considered. DPP did however occur in concentrations above its PNEC in River Viskan and concentrations of DPP and DCHA in the different effluents did at some occasions exceed the PNEC undiluted. No toxicity or ecotoxicity data has been found for any of the benzotriazole substances in the available literature. Any risk estimates have therefore not been carried out.

2 Sammanfattning

En screeningundersökning av bensotiazoler, bensendiaminer, dicyclohexylamin och bensotriazoler har genomförts inom ramen för Naturvårdsverkets screeningprogram.

Avsikten med en screeningundersökning är att bestämma koncentrationer av de utvalda substanserna i olika delar av den svenska miljön och därigenom belysa viktiga emissions- och transportvägar.

Denna undersökning har genomförts i samarbete med forskningsprogrammet ChEmiTecs "Organic Chemicals Emitted from Technosphere Articles" (www.chemitecs.se) finansierat av Naturvårdsverket. Målet med Chemitecs är att öka kunskapen om emissioner av organiska ämnen från varor. Resultaten ska stödja utvecklingen av svenska och europeiska handlingsprogram som ska minska riskerna med särskilt farliga ämnen.

Bensotiazolerna MBT, CBS, DBS och DBD fanns i en eller flera av de undersökta provtyperna. Detektionsfrekvenserna varierade både mellan substanserna och provtyperna. Fördelningsmönstret påverkades troligen både av föreningarnas egenskaper, såsom kemisk stabilitet och tendens att fördelas mellan olika faser, och av användningen. MBT hade högst detektionsfrekvens medan de andra bensotiazolerna hittades mera sporadiskt. En viktig spridningsväg till miljön för MBT är via reningsverk vilket pekar på diffusa emissioner från konsumentprodukter. Förekomst i dagvatten indikerar trafik-relaterade emissioner. MBT och övriga bensotiazoler förekom främst i vattenmiljön medan lufttransport verkar vara av mindre betydelse.

Bensendiaminen DPP hittades i vissa fall i till exempel ytvatten, dagvatten och reningsverksslam.

DCHA var vanligt förekommande i alla provtyper utom i gröda. Att DCHA återfinns i luft och deposition indikerar att substansen emitteras till luft och att lufttransport är en viktig spridningsväg. Förekomsten i dagvatten och i jord visar att trafikrelaterade emissioner är viktiga. DCHA hittades emellertid inte i gröda insamlad i närheten av trafikerade vägar. En annan viktig spridningsväg för DCHA är via reningsverk vilket antyder diffusa emissioner från till exempel konsumentprodukter

Bensotriazoler är vanligt förekommande i miljön både i bakgrundsmiljö och i urbana områden. Substanserna förekom i alla analyserade matriser: luft, deposition, ytvatten, sediment, jord och biota. Resultaten visade också att diffus spridning via reningsverk, deponier och dagvatten kan vara viktigt för förekomsten i miljön. Detta indikerar emissioner via användning av produkter. UVP är den bensotriazol som används mest följd av UV 328 och UV 327. Dessa substanser hittades också i högst koncentrationer.

I en enkel riskbedömning för vattenmiljöns pelagiska ekosystem identifierades inga större risker, dvs halterna var generellt lägre än PNEC i ytvatten och i avloppsvatten med hänsyn till förväntad utspädning. DPP förekom dock i koncentrationer över PNEC i Viskan.

Koncentrationen av DPP och DCHA i utspätt avloppsvatten överskred vid några tillfällen PNEC. Inga toxicitets eller ekotoxicitetsdata har hittats för någon av benzotriazolerna i tillgänglig litteratur. Några riskbedömningar för dessa har därför inte utförts.

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3 Introduction

A screening study of benzothiazoles, benzenediamines, dicyclohexylamine, and benzotriazoles has been carried out in the framework of the Swedish Environmental Protection Agency's screening program. The overall objective of a screening study is to determine the concentrations of the selected substances in a variety of media in the Swedish environment. Additional aims are to assess the possible emission sources and to highlight important transport pathways in the environment.

This screening has been carried out in collaboration with the research program ChEmiTecs "Organic Chemicals Emitted from Technosphere Articles" (www.chemitecs.se, financed by the Swedish Environmental Protection Agency). The aim of ChEmiTecs is to increase the scientific understanding of the magnitude of the problem regarding emissions of organic substances from articles with the objective to support policy development in Sweden and Europe.

A number of article and substance combinations have been selected as case studies in ChEmiTecs, which have been chosen based on trade volumes, field of application, chemical content, and risk issues. Chemical properties and predicted environmental effects of the chemicals have also been taken into account. Emissions from articles of the case study substances will be estimated in the ChEmiTecs program. However, there is a need to estimate emissions from articles in relation to other emission categories and pathways in order to dimension the problem. A lack of information concerning the presence in the environment of the selected case study chemicals has been identified why supplementary monitoring of these substances is needed. The selection of the chemicals for this screening was made in collaboration with the ChEmiTecs program. The results will be used in ChEmiTecs setting emission in relation to other sources and also for validation of models.

The substances included in this screening are benzothiazoles, benzenediamines and benzotriazoles. Benzothiazoles are used as accelerators in car tyres. Benzenediamines act as aging protection in car tyres. Benzotriazoles are used as UV-stabilizer in coated textile. The main pathway of these chemicals to the environment is supposed to be via emissions during the service life of articles used in the society.

In addition, dicyclohexylamine, DCHA, was included in the screening. A previous screening study has shown a widespread occurrence of this amine in the Swedish environment (Woldegiorgis et al., 2008). The results also indicated that diffuse dispersion of DCHA from traffic and other urban activities seem to be important for the occurrence in the environment. In addition DCHA has been identified as a possible degradation product of benzothiazoles.

This screening study has been carried out by IVL Swedish Environmental Research Institute (IVL) and Umeå University (UmU). The chemical analyses of benzothiazoles, benzenediamines and DCHA were made at IVL. Benzotriazoles were analysed at UmU.

4 Substances in the screening: Sources, pathways, properties and toxicity

4.1 Benzothiazoles, benzenediamines and dicyclohexylamine

4.1.1 Substances in the screening and their properties

The screening includes five benzothiazoles, two benzenediamines and dicyclohexylamine. The selected substances are specified in Table 1 where also CAS-numbers are given together with abbreviations and chemical structures.

Table 1: Substances included in the screening

Name	Abbreviation	CAS-number	Structure
Benzothiazoles			
Benzothiazole-2-thiole/ 2-Mercaptobenzothiazole	MBT	149-30-4	
N-tert-butylbenzothiazole-2-sulphenamide	TBS	95-31-8	
N-cyclohexylbenzothiazole-2-sulphenamide	CBS	95-33-0	
N,N-dicyclohexylbenzothiazole-2-sulphenamide	DBS	4979-32-2	
Di(benzothiazole-2-yl) disulphide	DBD	120-78-5	
Benzenediamines			
N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine	DPP	793-24-8	
N,N'-bis(1,4-dimethylpentyl)-1,4-benzenediamine	BBD	3081-14-9	
Dicyclohexylamine	DCHA	101-83-7	

Physical properties of the screened substances are listed in Table 2¹. These properties vary among the substances but in general they have low vapour pressure, *i.e.* are not volatile, low water solubility and relatively high octanol-water partitioning coefficient (K_{ow}); the latter meaning that these substances have potential to bioaccumulate in living organisms (except MBT as $\log K_{ow} < 3$).

Table 2: Physical properties of the benzothiazoles, benzenediamines and DCHA.

	Molecular formula	Molecular weight (g/mol)	Water solubility	Vapour pressure	Log K_{ow}
Benzothiazoles					
MBT	C7H5NS2	167.255	120 mg/L at 24°C (EXP) ^a	0.0619 Pa at 25°C (EST) ^a / 0.0003 Pa at 25°C ^b	2.42 (EXP) ^a
TBS	C11H14N2S2	238.378	0.3 mg/l ^b	0.000137 Pa at 25°C (EXP) ^b	4.38 (EXP) ^b , 4.67 ^b
CBS	C13H16N2S2	264.415	0.32 mg/L at 21°C ^c	1.5×10 ⁻⁶ Pa at 20°C ^c	4.93 ^c
DBS	C19H26N2S2	346.56	ca 30 mg/l ^b		
DBD	C14H8N2S4	332.495	10 mg/L at 25°C (EXP) ^a	3.39×10 ⁻⁸ Pa at 25°C (EST) ^a	4.66 (EST) ^a
Benzenediamines					
DPP	C18H24N2	268.402	0.0011 mg/L (not soluble) ^b		5.4 (EST) ^b
BBD	C20H36 N2	304.518			
DCHA					
DCHA	C12H23N	181.321	800 mg/L at 25°C ^b	4.51 Pa at 25°C (EXP) ^a	4.37 (EST) ^a / 3.5 (EST) ^b

a) ChemIDplus Advanced (<http://chem.sis.nlm.nih.gov/chemidplus/chemidheavy.jsp> 2011.05.25)

b) IUCLID Chemical Data Sheet (<http://ecb.jrc.ec.europa.eu/esis/> 2011.05.25)

c) EU Risk assessment report (<http://ecb.jrc.ec.europa.eu/esis/> 2011.05.25)

Expected environmental fate of the screened substances is described below. Unless otherwise stated the data was retrieved from the Hazardous Substances Data Bank (HSDB, see list of references), where specific references are given.

Benzothiazole-2-thiole (MBT) is generally rather persistent (Haroune et al., 2004). When released to soil, it has low mobility and a half-life of 92-248 days. When released to water MBT will partly dissociate but may also adsorb to sediment. In water it can be degraded photolytically with a half-life about 0.05 days in the summer and 0.21 days in the winter. When released to air, MBT reacts with the hydroxyl radical with an atmospheric half-life of 8.4 hours.

Di(benzothiazole-2-yl) disulphide (DBD) is immobile in soil and biodegradation is slow. In an aquatic system the substance can be expected to partition to sediment, there are indications that degradation is slow also in this media. It does however have the potential to undergo photolysis as it adsorbs UV light >290 nm. In the atmosphere DBD is readily degraded as it reacts with hydroxyl radicals; the estimated half-life is 1.3 hours.

¹ Data on substance properties were searched for in ChemIDplus Advanced and in ESIS (IUCLID Chemical Data Sheet and EU Risk Assessment Report)

Dicyclohexylamine (DCHA) is reported to undergo rapid photolysis (half-life of 2.9 hours, OECD 2006) but since it has a high $\log K_{ow}$ -value it will probably mostly be abundant in sediment and soil and hence not be exposed to sunlight. Due to its relatively high vapour pressure DCHA can volatilize from moist soil and water surfaces. In the atmosphere the substance is readily degraded with an estimated half-life of 2.9 hours due to reaction with hydroxyl radicals. It is very corrosive and reactive with acids, oxidizing agents and chloroformates. In microbial degradation studies with active sludge DCHA has shown to be readily biodegradable (OECD 2006).

For N-tert-butylbenzothiazole-2-sulphenamide (TBS), N-cyclohexylbenzothiazole-2-sulphenamide (CBS), N,N-dicyclohexylbenzothiazole-2-sulphenamide (DBS), N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (DPP) and N,N'-bis(1,4-dimethylpentyl)-1,4-benzenediamine (BBD) no data were found in the HSDB regarding the environmental fate.

4.1.2 Production and usages

One of the major uses of benzothiazoles is as accelerators in rubber vulcanization (HSDB 2011). The volumes of benzothiazoles used in chemical products in Sweden between 1999 and 2008 are given in Figure 1 (TBS, CBS, DBD) and Figure 2 (MBT) (KemI 2011, SPIN database), data for DBS is confidential. Taken together the greatest amounts were used in 1999 and decreased in 2000, but since then no further decrease could be observed. The volumes given do not include chemical products with confidential volume information or the volume of benzothiazoles in pesticides.

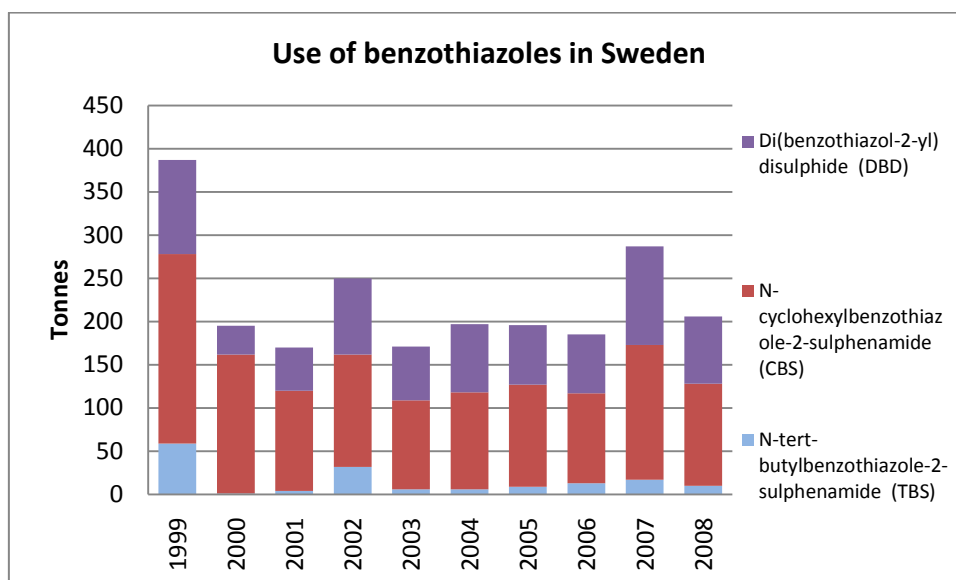


Figure 1: The use of benzothiazoles in Sweden. Data for N,N-dicyclohexylbenzothiazole-2-sulphenamide (DBS) was not available (SPIN database, KemI, 2011).

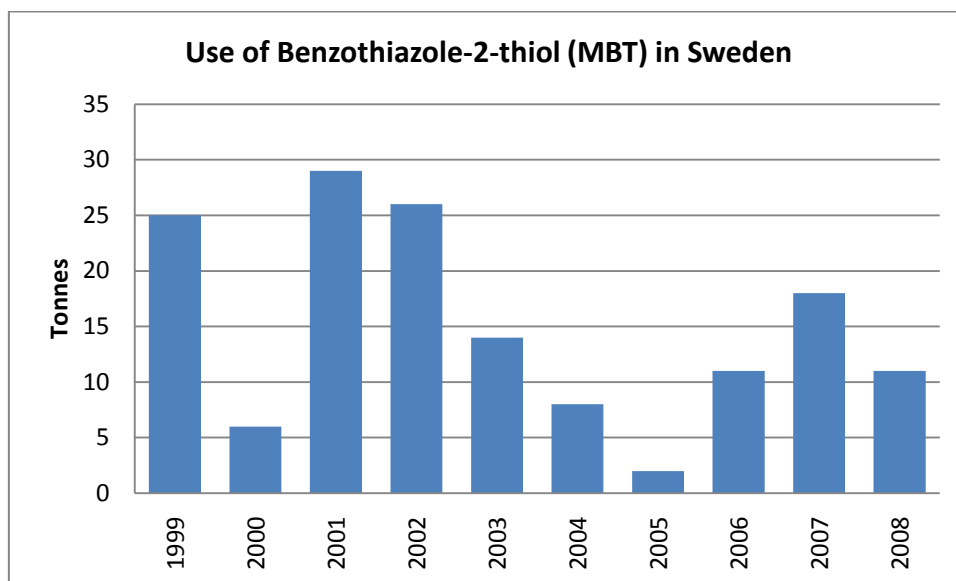


Figure 2: The use of benzothiazole-2-thiol (MBT) in Sweden (SPIN database, KemI, 2011).

MBT is an accelerator in car tyres, both direct but also indirect as a degradation product from other accelerators (see above). It is a HPV chemical with registered production in Germany, Netherlands, Belgium, Spain, France and UK (ESIS, 2011). MBT also has applications such as inhibiting bio-corrosion in cooling systems or in paper manufacturing (Remberger 2006). The substance is a biocide and as such included in the European directive on biocides EG 2032/2003.

CBS is a HPV chemical that is one of the most common accelerators in today's tyre industry. CBS has according to the chemical products register the highest use in Sweden of the four benzothiazoles (Figure 1); more than 100 tonnes was used annually in chemical products.

DBS is a high production volume (HPV) chemical with confidential use in Sweden. This chemical may degrade in the environment to form MBT. Another possible degradation product of DBS is DCHA.

TBS and **DBD** are used in chemical products in significant volumes in Sweden (Figure 1). Both substances are used as rubber accelerators, in addition DBD is used as a retarder in neoprene and plasticiser/retarder in polychloroprene (HSDB 2011).

As benzothiazoles are accelerators that are common in tyre manufacturing large quantities of these substances are imported from abroad with tyres. During the period 2006-2009, the accumulated amount of tires (net inflow) used for cars, lorries and buses and tractors in Sweden was 29 million, 11 million and 2.2 million, respectively. The net inflow was calculated using data on import and export and domestic production when available (Brolinson and Carlsson, 2011).

Benzenediamines are used as aging protection in car tyres. Like the benzothiazoles these chemicals enter Sweden in car tyres (Einarson, 2009). Two chemicals were identified as representatives for this substance group; DPP and BBD.

DPP is a HPV chemical commonly found in rubber products. The usage volumes in chemical products in Sweden 1999-2008 are given in Figure 3 (KemI 2011, SPIN database). The use of DPP in chemical products was about 150 tonnes per year in recent years.

BBD volume used in chemical products in Sweden is confidential.

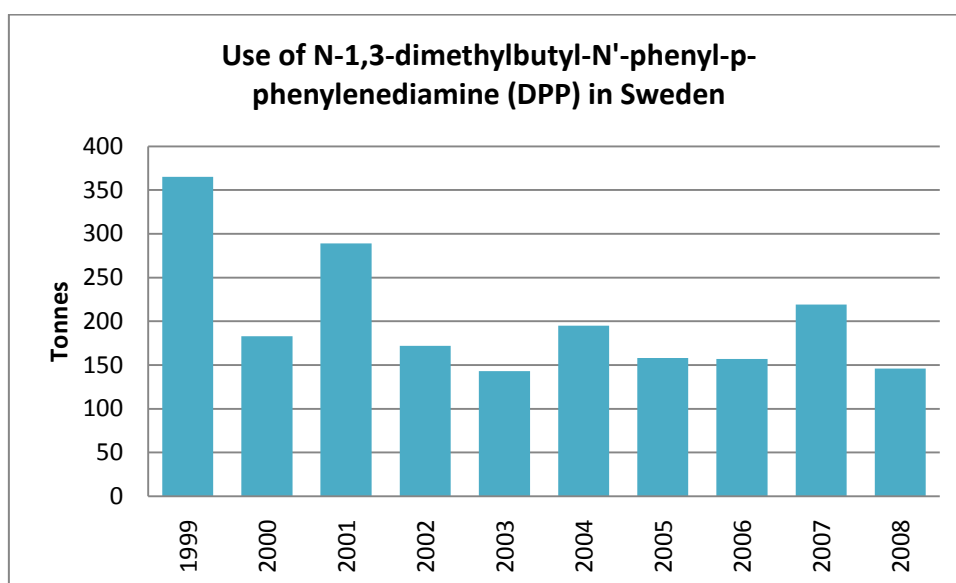


Figure 3: The use N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (DPP) in Sweden. Data for 1,4-Benzenediamine, N,N'-bis(1,4-dimethylpentyl)- (BDD) is confidential in the database (SPIN database, KemI, 2011).

DCHA has a wide use in chemical processes. It is a hydrophobic amine used in insecticides, plasticizers, in the metal industry, as a fuel oil additive and as a chemical intermediate. It is associated with traffic since it is a component used in the rubber vulcanization process. It could also be a degradation product from accelerators such as DBS (see above). The usage volumes in chemical products in Sweden between 1999 and 2008 are given in Figure 4. According to the SPIN database about 20 tonnes was used in Sweden during the recent years.

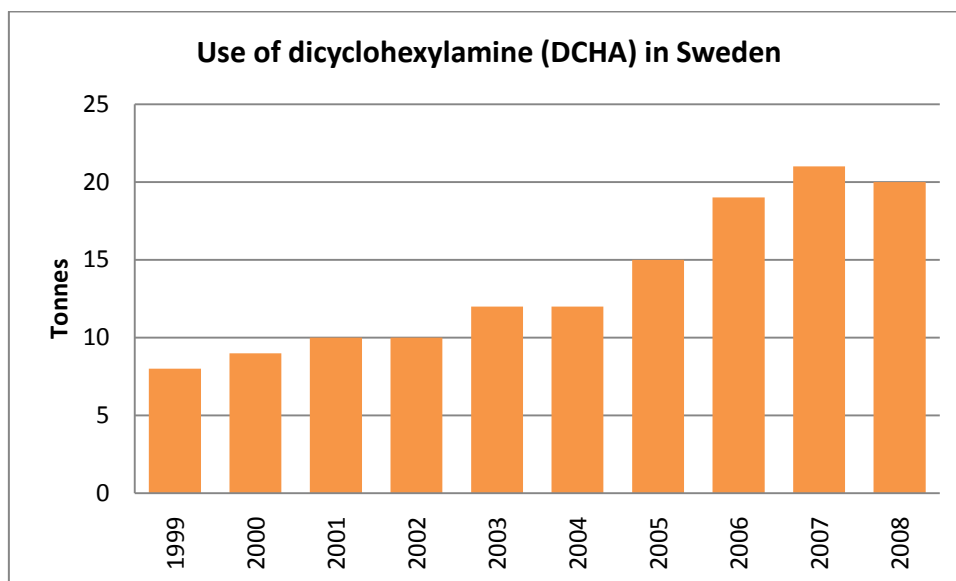


Figure 4: The use of DCHA in Sweden (SPIN database, KemI, 2011).

4.1.3 Occurrence - Previous measurements

Occurrence of the substances included in this screening as found in previous investigations are presented below and concentrations in different media are presented in Table 3.

In a previous screening **MBT** was found in environmental matrixes in an urban area, Stockholm, as well as in effluent and sludge from wastewater treatment plants (WWTPs) (Remberger et al 2006). The occurrence of MBT in waste water from Germany has also been shown (Kloepfer et al., 2005).

CBS has previously been investigated in Japan, with focus on urban environments, where it was found in varying concentrations in matrixes such as runoff water and road dust (Kumata et al., 2002).

A previous screening has shown that **DCHA** was widely distributed in the Swedish environment; out of 95 samples included in the study DCHA was detected in 74 (78 %). DCHA was detected in all sampled matrixes and practically at all types of sampling locations (Woldegiorgis et al., 2008). The authors of the study concluded that diffuse urban emissions were important for the occurrence of the substance in the environment.

Environmental data for the benzothiazoles: TBS, DBS and DBD and the benzenediamines: DPP and BBD were not found.

A literature study on the occurrence of the case study chemicals in the environment, which included benzothiazoles and benzenediamines, has also been carried out within the ChEmiTecs project (Paulson, 2010). A conclusion from this study was that there was a general lack of data for these chemicals in the scientific literature.

Table 3: Occurrence of benzothiazoles, benzenediamines and dicyclohexylamine, results from previous measurements.

Substance	Occurrence	Concentration levels	Reference
Benzothiazole-2-thiol (MBT)	Air (urban and close to poss. point source)	<1 ng/m ³ , n=6	Remberger et al., 2006
	Atmospheric deposition	<5-37 ng/m ² day, n=3	
	Surface water	<0.05-0.08 µg/l, n=13	
	Biota (perch)	<10 µg/kg ww, n=7	
	Sediments	<20-70 µg/kg DW, n=16	
	WWTP Influent	0.02-0.19 µg/l	Kloepfer et al., 2005
	WWTP Effluent	0.01-0.04 µg/l	
	WWTP effluent	<0.05-0.63 µg/l, n=13	Remberger et al., 2006
	WWTP Sludge	<20-950 µg/kg DW, n=24	
	Water, leachate from landfill	<0.05-0.11 µg/l, n=3	
	Water, leachate before treatment	<0.5 µg/l, n=1	
	Water, leachate after treatment	11 µg/l, n=1	
Water, leachate after aeration pond	18 µg/l, n=1		
N-cyclohexyl-benzothiazole-2-sulphenamide (CBS)	Runoff water	22-510 ng/l	Kumata et al., 2002
	Aquatic sediments	2.3-17 ng/g, n=20	
	Urban environment, Tokyo: tire tread	1400-14000 ng/g DW, n=4	
	Urban environment, Tokyo: Road dust, outside tunnel	87-440 ng/g DW, n=7	
	Urban environment, Tokyo: Road dust, inside tunnel	15-73 ng/g DW, n=9	
	Urban environment, Tokyo: Runoff	10-41 ng/l	
	Urban environment, Tokyo: Road dust, outside tunnel	137-1200 ng/g DW, n=7	
	Urban environment, Tokyo: Road dust, inside tunnel	27-220 ng/g DW, n=9	
Dicyclohexylamine (DCHA)	Urban environment, Tokyo: River sediments	3.2-16 ng/g DW, n=8	Woldegiorgis et al., 2008
	Air (background)	26-230 pg/m ³ , n=3	
	Air (urban background)	23-380 pg/m ³ , n=6	
	Soil (background)	50 ng/g, n=1	
	Soil (urban)	1.7-70 ng/g, n=3	
	Soil (point source)	0.86-49 ng/g, n=6	
	Sediments (limnic)	<3.3 ng/g DW, n=5	
	Sediments (coast)	<2.3-3.6 ng/g DW, n=3	
	Water (coast)	<5.4-2.7 ng/L, n=3	
	Water (limnic)	<5.4 ng/L, n=5	
	Ground water	<5.4-3.9 ng/L, n=4	
	Water (influent WWTP)	<11-76 ng/L, n=8	
	Water (effluent WWTP)	<5.4-140 ng/L, n=11	
	Sludge (WWTP)	5.1-770 ng/g DW, n=13	
	Storm water	<5.4-940 ng/L, n=20	
Leachate landfills	<5.4-1300 ng/L, n=3		

4.1.4 Toxicity

Molander (2010) made a literature review of described (eco)toxicity for the substances included in the screening (excluding DCHA). The review is summarized below. For more detailed descriptions the reader is referred to the original report. For BBD no data was found in the publicly available literature.

For most of the substances for which data were found, toxic effects in both mammals and aquatic organisms have been reported. The acute toxicity to rodents was low to moderate. Repeated doses did however give effects on *e.g.* kidneys and liver. Some of these substances

may also be harmful to reproduction or development. For a few substances there was also an indication of mutagenicity and/or cancerogenicity. The majority of the substances (for which data were found) were acutely toxic to aquatic organisms and some of them may also cause long-term negative effects in the aquatic environment. Several of the substances degrade to toxic metabolites, which makes it important to include also these transformation products in a risk assessment. Classification and labelling for the substances having such information is given in Table 4.

Table 4: Harmonized classification and labelling for some benzothiazoles and dicyclohexylamine (table 3.2, in annex I to Directive 67/548/EEC)

Substance	Classification and labelling
Benzothiazole-2-thiole / 2-mercaptobenzothiazole (MBT)	Classified as R43, N; R50-53 Labelled as Xi,N; R43-50/53, S(2)-24-37-60-61
N-cyclohexylbenzothiazole-2-sulphenamide (CBS)	Classified as R43, N; R50-53 Proposed classification: Category 3 reprotoxicity, R62: Possible risk of impaired fertility (EU, 2008a) Labelled as Xi,N; R43-50/53, S(2)-24-37-60-61
Di(benzothiazol-2-yl) disulphide (DBD)	Classified as R31, R43, N; R50-53 Labelled as Xi,N; R31-43-50/53, S(2)-36/37-60-61
Dicyclohexylamine (DCHA)	Classified as Xn; R22 C; R34 N; R50-53 Labelled as C; N; R: 22-34-50/53; S: (1/2-)26-36/37/39-45-60-61 Concentration limits: C; R34: C ≥ 10 %; Xi; R36/38: 2 % ≤ C < 10 %

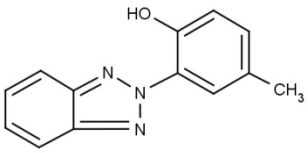
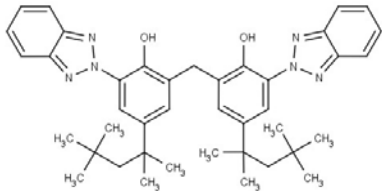
4.2 Benzotriazoles

4.2.1 Substances in the screening and their properties

The screening includes seven benzotriazoles which are shown in Table 5 were also IUPAC names, CAS-numbers, abbreviations and chemical structures are given.

Table 5: Substances included in the screening, CAS-number, abbreviations and chemical structure.

Name	Abbreviation	CAS-number	Structure
2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol IUPAC Name: 2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol	UV-328	25973-55-1	
2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol IUPAC Name: 2-(benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol	UV-329	3147-75-9	
2-(benzotriazol-2-yl)-4,6-di-tert-butylphenol IUPAC Name: 2-(2'-Hydroxy-3',5'-di-tert-butylphenyl)benzotriazole	UV-320	3846-71-7	
2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol IUPAC Name: 2,4-ditert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol	UV-327	3864-99-1	
2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol IUPAC Name: 2-(benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenol	UV-234	70321-86-7	

Name	Abbreviation	CAS-number	Structure
2-(benzotriazol-2-yl)-4-methylphenol IUPAC Name: 2-(2-Hydroxy-5-methylphenyl)benzotriazole	UV-P	2440-22-4	
2,2'-Methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol] IUPAC Name: 2,2'-Methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol]	UV-360	103597-45-1	

Physical properties of the substances are listed in Table 6. Data on substance properties were only found for **UV-328** and **UV-P**, the first with rather low water solubility and vapour pressure but a high predicted partition coefficient between water and octanol (K_{ow}) and the latter with higher water solubility and vapour pressure but lower $\log K_{ow}$.

Table 6: Physical properties of the benzotriazoles. All data from (a).

	Molecular formula	Molecular weight (g/mol)	Water solubility	Vapour pressure	Log K_{ow}
UV-328	C22H29N3O	351.491	0.015 mg/L at 25°C (EST)	2.573×10^{-8} Pa at 25°C (EST)	7.250 (EST)
UV-329	C20H25N3O	323.438			
UV-320	C20H25N3O	323.438			
UV-327	C20H24ClN3O	357.883			
UV-234	C30H29N3O	447.579			
UV-P	C13H11N3O	225.25	25.6 mg/L at 25°C (EST)	1.06×10^{-5} Pa at 25°C (EST)	4.31 (EXP)
UV-360	C41H50N6O2	658.886			

a) ChemIDplus Advanced (<http://chem.sis.nlm.nih.gov/chemidplus/chemidheavy.jsp> 2011.06.07)

In the hazardous substances data bank (HSDB, see list of references) data on the environmental fate were not found for any of the benzotriazoles.

4.2.2 Production and usages

Benzotriazoles are used as UV stabilizers in coated textiles. These types of chemicals go under the collective trade name “*Tinuvin*” and have been pointed out by the ChEmiTecs program as an interesting group for studies of the environmental fate. Benzotriazoles may to a large extent enter Sweden through imported finished goods, which make these stabilizers interesting chemicals in ChEmiTecs.

The use of benzotriazoles in chemical products in Sweden between 1999 and 2008, according to the Swedish product register is shown in Figure 5 (KemI 2011, SPIN database). The information on the usage of **UV-360** and **UV-320** is confidential. The greatest amounts, 57 tonnes, were used in 1999 but no decreasing trend can be seen over

the time period 1999-2008. **UV-P** is the benzotriazole with highest usage volumes, 24 to 40 tonnes/year.

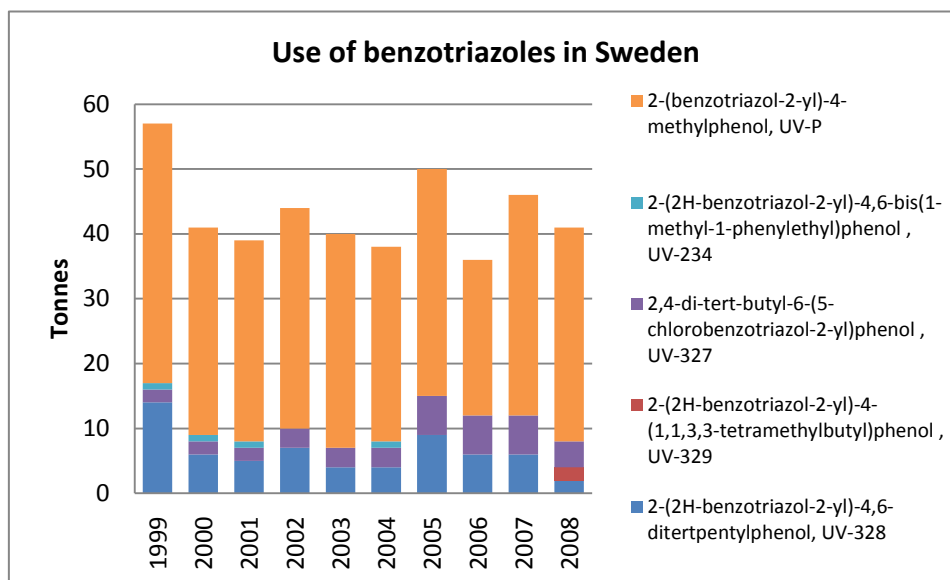


Figure 5 The use of benzotriazoles in Sweden. The usage of Phenol, 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)- (UV-360) and 2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320) in Sweden is confidential (SPIN database, KemI, 2011)

4.2.3 Occurrence - Previous measurements

Occurrence in the environment of the substances included in this screening as found in previous investigations are presented below. Concentrations in different media are presented in Table 7.

The occurrence of the benzotriazoles has primarily been studied in the Japanese environment. Water contaminant levels vary greatly between various rivers and range from not detected to 5 µg/L depending on substance and river/stream. The benzotriazoles were frequently found in sediments in the µg/kg range. Based on the sediment data it may be concluded that UV-328, UV-329, and UV-234 are the most abundant benzotriazoles in the Japanese environment. These are also used in significant quantities in Sweden, see Figure 5. However, the benzotriazole most used in Sweden, UV-P, were detected at lower levels.

Samples from waste water treatment plants were also included in the Japanese studies. Levels in the low ng/g range were reported both in influent and effluent water, which indicates an inefficient removal of these substances in the WWTP process. Parts of the benzotriazoles were however removed from the water as levels in the 100-ng/g range were reported for sewage sludge (dry weight basis).

Table 7: Occurrence of benzotriazoles, from previous measurements.

Substance	Occurrence found	Concentration levels	Reference
2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)	Fish (whole, 5 species)	0.19-0.29 ng/g WW	Nakata et al., 2009
	Streams (Japan)	70 ng/L, n=1	Kameda et al., 2011
	Heavily polluted rivers (Japan)	149-4780 ng/L, n=4	
	Moderately polluted rivers (Japan)	30-583 ng/L, n=8	
	Sediments Ariake Sea	2.6-16 ng/g DW, n=11	Nakata et al., 2009
	Sediments Omuta River	18-320 ng/g DW, n=5	Kameda et al., 2011
	Sediments, streams (Japan)	10-1146 µg/kg DW, n=2	
	Sediments, heavily polluted rivers (Japan)	21-1735 µg/kg DW, n=6	
	Sediments, moderately polluted rivers (Japan)	10-213 µg/kg DW, n=9	
	Sediments, rivers (Background sites, Japan)	29-89 µg/kg DW, n=3	
	Sediments, WWTP Effluent outflow (Japan)	10-85 µg/kg DW, n=3	
	Influent WWTP	14-23 ng/L, n=5	Nakata and Shinohara, 2010
	Influent WWTP	34 +/- 15 ng/L, n=9	
	WWTP Effluent	2.6 +/- 0.32 ng/L, n=5	Kameda et al., 2011
WWTP Effluent (Japan)	47-88 ng/L, n=3		
Sludge	510 +/- 67 ng/g DW, n=10	Nakata and Shinohara, 2010	
2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV-329)	Sediments, streams (Japan)	16 µg/kg DW, n=1	Kameda et al., 2011
	Sediments, heavily polluted rivers (Japan)	7.4-269 µg/kg DW, n=3	
	Sediments, moderately polluted rivers (Japan)	1.1-4.3 µg/kg DW, n=3	
2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)	Fish (whole, 5 species)	<0.05-0.06 ng/g WW	Nakata et al., 2009
	Sediments Ariake Sea	0.3-2.3 ng/g DW, n=11	
	Sediments Omuta River	2.6-14 ng/g DW, n=5	
2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol (UV-327)	Fish (whole, 5 species)	0.29-0.51 ng/g WW	Nakata et al., 2010
	Sediments Ariake Sea	1.6-9.9 ng/g DW, n=11	
	Biota: finless porpoises (bubber)	19 ± 19 ng/g lipid WW	
	Streams (Japan)	5 ng/L, n=1	Kameda et al., 2011
	Moderately polluted rivers (Japan)	1-6 ng/L, n=6	
	Heavily polluted rivers (Japan)	1 ng/L, n=1	Nakata et al., 2009
	Sediments Omuta River	16-190 ng/g DW, n=5	
	Sediments, rivers (Background sites, Japan)	0.5-1.1 µg/kg DW, n=2	
	Sediments, streams (Japan)	0.6-37 µg/kg DW, n=2	
	Sediments, moderately polluted rivers (Japan)	0.4-2.6 µg/kg DW, n=10	
	Sediments, heavily polluted rivers (Japan)	0.7-18 µg/kg DW, n=5	
	Sediments, WWTP Effluent outflow (Japan)	0.3-1.05 µg/kg DW, n=4	Nakata and Shinohara, 2010
	Influent WWTP	5.6-20 ng/L, n=5	
	Effluent	<8.7 ng/L, n=5	
Sludge	170 +/- 33 ng/g DW, n=10		
WWTP Effluent (Japan)	2 ng/L, n=1	Kameda et al., 2011	
2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (UV-234)	Sediments, rivers (Background sites, Japan)	8.3-315 µg/kg DW, n=3	Kameda et al., 2011
	Sediments, streams (Japan)	1266 µg/kg DW, n=1	
	Sediments, moderately polluted rivers (Japan)	18-315 µg/kg DW, n=8	
	Sediments, heavily polluted rivers (Japan)	33-324 µg/kg DW, n=4	
2-(benzotriazol-2-yl)-4-methylphenol (UV-P)	Streams (Japan)	10 ng/L, n=1	Kameda et al., 2011
	Moderately polluted rivers (Japan)	2 ng/L, n=1	
	Sediments, rivers (Background sites, Japan)	1.3 µg/kg DW, n=1	
	Sediments, streams (Japan)	15 µg/kg DW, n=1	
	Sediments, moderately polluted rivers (Japan)	0.5-3.3 µg/kg DW, n=2	
	Sediments, heavily polluted rivers (Japan)	2.6-4.4 µg/kg DW, n=2	
WWTP Effluent (Japan)	3-23 ng/L, n=3		

4.2.4 Toxicity

Molander (2010) did not find any toxicity or ecotoxicity data for any of the benzotriazole substances in the available literature.

5 Sampling programme

A sampling strategy was developed in order to determine concentrations of the selected substances in different matrices in the Swedish environment. The measurements also aimed to identify major emission sources, important transport pathways in the environment and possible uptake in biota. The sampling programme of the different substance groups was coordinated as much as possible; however there are differences in emission sources and pathways among the different groups why the sampling programs to some extent differ.

An overview of the sampling programme for benzothiazoles, benzenediamines and dicyclohexylamine is given in Table 8. Due to the findings in a previous screening of DCHA (Woldegiorgis et al., 2007) the initial programme was supplemented with biota samples, both from the aquatic and terrestrial environment. The sampling programme for benzotriazoles is shown in Table 9. A detailed description of the samples is given in Appendix 1.

As the substances included in this screening are related mainly to uses in articles and products, emissions via diffuse sources were identified as the main pathway of these chemicals to the environment. The sampling programme was therefore focused on emissions in urban environments. The measurements were carried out in an area with high population density - Stockholm. Some measurements were also undertaken in a smaller city - Borås. Two sites at the Swedish west coast were chosen as potential point sources, Stenungsund, a dense industrial area, and Lysekil nearby an oil refinery.

The measurements in the urban environment included air (gas- and particle phases), atmospheric deposition, storm water and soil as well as samples from the aquatic environment, surface water, sediment and biota.

Diffusive emissions from the society was studied by analysing effluent water and sludge from municipal waste water treatment plants (WWTPs) and waste water from landfills.

Roads and traffic were identified as potential emission sources and therefore soil- and biota (crop) samples were collected close to busy roads.

Biota samples, mussels and fish, were collected in the areas of Stockholm, Stenungsund and Lysekil.

In order to investigate environmental background levels of the chemicals air, deposition sediment, soil and biota samples were collected at background sites at different locations in Sweden. The air- and deposition measurements were carried out at Råö, a background station at the Swedish West coast. The measurements at Råö were co-ordinated with measurements carried out within the Swedish Monitoring Programme for Air Pollutants.

Table 8: Sampling programme – benzothiazoles, benzenediamines and dicyclohexylamine. Number of samples at the different sampling stations.

	Air	Atm. deposition	Sediment	Biota	Crops	Soil	Surface water	Effluent, landfill	Effluent, WWTP	Sludge, WWTP	Storm water	Total
Background sites												
Råö	2	2										4
Gårdsjön			1	1		1	1					4
Tärnan			1	1			1					3
Sandsjön			1	1			1					3
Fjällbacka				1								1
Nidingen				1								1
Grebbestad				1								1
Urban sites												
Stockholm, Valhallavägen	2	2				1						5
Stockholm, Humlegården						1						
Stockholm, Årstaviken			1	1			1					3
Stockholm, Käppala WWTP								1		1		2
Stockholm, Henriksdal WWTP								1		1		2
Stockholm, Henriksdal				1								1
Stockholm, Huddinge											2	2
Stockholm, Årsta											2	2
Stockholm, Långholmen/Riddarfjärden			1	1								2
Stockholm, Stora Essingen			1									1
Stockholm, Riddarfjärden							1					1
Stockholm, Biskopsudden				1								1
Stockholm, Torsbyfjärden				1								1
Stockholm, Görveln							1					1
Stockholm, Norsborg							1					1
Borås	2						2					4
Borås, Gässlösa WWTP								1		1		2
Umeå, Öhn WWTP								1		1		2
Göteborg, Ryaverken WWTP								1		1		2
Potential point sources												
Stockholm, Ekerö					4							4
Stockholm, Salem						3						3
Stenungsund	2			5			2					9
Lysekil				3								3
Landfill									3			3
Total	8	4	6	14	4	6	11	5	3	5	4	74

Table 9: Sampling programme – Benzotriazoles. Number of samples at the different sampling stations

	Air	Atm. dep.	Sediment	Biota	Soil	Surface water	Effluent landfill	Effluent, WWTP	Storm water	WWTP sludge	Total
Background sites											
Råö	2	2									4
Gårdsjön			1	1	1	1					4
Tärnan			1			1					2
Sandsjön			1	1							2
Urban sites											
Stockholm, Valhallavägen	2	2			2						6
Stockholm, Årstaviken			1	1		1					3
Käppala WWTP								1		1	2
Stockholm, Henriksdal WWTP								1		1	2
Stockholm, Huddinge									1		1
Stockholm, Årsta									1		1
Stockholm, Långholmen/Riddarfjärden			1	1							2
Stockholm, Stora Essingen			1								1
Stockholm, Riddarfjärden						1					1
Borås	2					2			2		6
Borås, Gässlösa WWTP								1		1	2
Umeå, Öhn WWTP								1		1	2
Göteborg, Ryaverken WWTP										1	1
Bollebygd WWTP								1		1	2
Ellinge WWTP								1		1	2
Nolhaga WWTP										1	1
Potential point sources											
Stockholm, Salem					1						1
Stenungsund	2										2
Landfill							4				4
Total	8	4	6	4	4	6	4	6	4	8	54

6 Methods

6.1 Sampling

Air: The atmospheric samples were collected using a high volume air sampler (HVS). A glass fibre filter was used for trapping the particles followed by an polyurethane foam (PUF) adsorbent for collecting compounds in the gas phase. The air sampling was carried out weekly and sample extracts were then combined to represent longer time periods.

Deposition: Both wet and dry deposition was collected using an open sampler (bulk sampler). This sampler consists of a 1 m² Teflon coated surface with 10 cm high edges. The bottom declines slightly to a central opening where a cassette with a PUF adsorbent is attached. After sampling the adsorbent is removed and the surface cleaned using fibre glass filters and ethanol. The deposition sample includes both compounds in the precipitation and compounds deposited to the collection surface of the sampler (PUF, filters and ethanol). Both the precipitation and the deposited particles are included in the analysis. The deposition sampling was carried out weekly and sample extracts was then combined to represent longer time periods.

Soil: The upper 2-3 cm of surface soil was collected in glass jars and stored in a freezer until the analysis.

Crops: Straws of wheat were cut with pruning shears, collected in plastic bags and stored in a freezer (-18°C) until analysed.

Surface water was collected in glass bottles and stored at 6 °C until analysed.

Sediment: Surface sediments (0-2 cm) samples were collected by means of a Kajak sampler. The sediment was transferred into muffled (400 °C) glass jars and stored in a freezer (-20 °C) until analysed.

Fish were collected by means of fishing nets. The net fishing in Stockholm was approved by the fishery authorities in Stockholm and the ethical board for animal testing in northern Stockholm (D. no. 527/07). The fish samples were wrapped in pre-cleaned aluminium foil and stored in a freezer (-18°C) until analysed. The fish samples from Sandsjön and Tärnan was provided and prepared by the Swedish museum of Natural History.

Blue mussels: Samples from two background sites were provided from the Swedish Museum of Natural History. Blue mussels (10-30 per site) were collected from five sites in the vicinity of Stenungsund. The samples were provided by the Environmental Health Unit at the municipality of Stenungsund. Samples from the vicinity of Lysekil were provided by Preemraff Lysekil. At the laboratory, the mussels were collected in glass jars and stored in freezer (-18°C) until analyses.

Effluent water: The staff at the different WWTPs collected effluent water samples in 1 litre dark glass bottles. The sample was acidified to pH 3 using H_3PO_4 and stored at 6 °C.

WWTP sludge: The staff at the different WWTPs collected de-watered sludge samples from the anaerobic chambers. The sludge was transferred into glass jars and stored in a freezer (-18 °C) until analysed. All glass equipment used was muffled (400 °C) before use.

Effluent water from landfills was collected in 1 litre glass bottles.

Storm water samples were collected in 1 litre glass bottles and stored at 6 °C. The samples were provided by the local Traffic Offices in Stockholm and Borås.

6.2 Analysis

Air and deposition samples were extracted in accordance with the methods used in the monitoring program for air pollutants. Therefore all air and deposition samples were Soxhlet extracted at IVL. The samples (PUF-plugs and filters) were Soxhlet extracted with acetone for 24 hours (+/- 2 hours). Extracts from the adsorbent and filter were combined and divided for determination of the different substance groups, according to Figure 6.

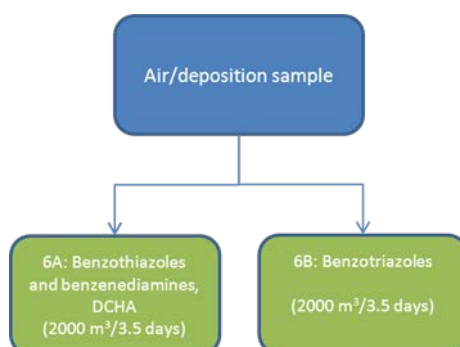


Figure 6 A schematic picture showing how the air and deposition extracts were split prior to analysis.

6.2.1 Benzothiazoles, benzenediamines and dicyclohexylamine

6.2.1.1 Air and deposition sample clean-up.

An internal standard (coumatetralyl) was added to the combined sample extracts. The extracts were then concentrated on a Rotavapor EL131 (Büchi) and diluted with ultra-pure water. The sample clean-up was performed using the same procedures as for water samples (see below).

6.2.1.2 Water sample clean-up

Water samples, 100-500 ml depending on sample type, were spiked with coumatetralyl as internal standard (IS) prior to filtration. The filtrate was concentrated on a SPE-column (Isolute C18, 100mg), activated with methanol and ultra-pure water. The cartridge was washed with ultra-pure water and dried for 5 min under vacuum. The SPE-column was eluted with methanol followed by hexane and the extract concentrated under a stream of

nitrogen. Sulphamethoxazole was added as volumetric standard (VS) and the extract was transferred to a vial and stored in a freezer until HPLC-MS analysis.

6.2.1.3 Sediment and soil sample clean-up

Freeze dried and thawed solid samples were spiked with coumatetralyl as IS prior to extraction. The sample was extracted twice with methanol via shaking. The combined extracts were centrifuged and the supernatant was concentrated under a stream of nitrogen. The extract was further centrifuged and sulphamethoxazole was added as VS before the extract was transferred to a vial and stored in a freezer until HPLC-MS analysis.

6.2.1.4 Crop sample clean-up

Thawed wet samples were spiked with coumatetralyl as IS prior to extraction. The sample clean-up was performed using the same procedures as for the sediment and soil samples.

6.2.1.5 Fish, mussel and sludge sample clean-up

Freeze dried and thawed samples were spiked with coumatetralyl as IS prior to extraction. The sample was extracted twice with methanol via shaking. Magnesium nitrate ($\text{Mg}[\text{NO}_3]_2$) was added to the combined extracts to precipitate fatty acids. The extract was centrifuged and the supernatant was concentrated under a stream of nitrogen. The extract was further centrifuged and sulphamethoxazole was added as VS before the extract was transferred to a vial and stored in a freezer until HPLC-MS analysis.

6.2.1.6 HPLC/MS analysis

Determination of the selected compounds were performed with an UFLC liquid chromatography system (Shimadzu Scientific Instruments, Columbia, USA), equipped with an autosampler, a quaternary pump, and on-line degassing system. The compound separation was performed with a reversed phase C_8 column (Thermo Scientific, HvPURITY C8, 3.0 mm ID x 50 mm length, 5 μm). Gradient elution was performed with 5 mM acetic acid and 5 mM ammonium acetate in water as solvent A and methanol as solvent B. The analytical detector was a triple quadrupole mass spectrometer, API 4000 LC/MS/MS system (Applied Biosystems, California, USA). The instrument altered between positive and negative mode during detection. The mass spectrometer interface was an electrospray ionization (ESI) source. The data processing and instrument (HPLC) control were performed by the Analyst software.

Table 10: Molecular ion, major fragments and limit of detection

Compound	{M+H} ⁺	{M-H} ⁻	Major fragments	Limit of detection (S/N=3)
MBT		166.0	134.0/88.0	*
TBS	-	-	-/-	-
CBS	265.0	-	183.1/166.1	*
DBS	347.1	-	180.2/138.2	*
DBD	333.1	-	167.1/123.2	*
DPP	-	-	-/-	-
BBD	269.1	-	185.1/184.1	*
DCHA	182.2	-	100.0/83.0	*
Coumatetralyl (IS)	-	291.0	141.0/-	-
Sulphamethoxazole (VS)	252.0	-	155.6/-	-

* Specified for each sample in Appendix 2

6.2.2 Benzotriazoles

6.2.2.1 Air and deposition sample clean-up.

The extracts (6B in Figure 6A) were then concentrated on a Rotavapor (Büchi) and diluted with methanol. This was repeated until only methanol remained. A subsample was transferred to a 2 ml vial and an internal standard, labelled simazine, was added and then analysed on the LC-MS system.

6.2.2.2 Water sample clean-up

From the water samples, 100-1000 ml depending on sample type, subsamples of about 10 ml were taken and spiked with labelled simazine as internal standard (IS) after filtration. The pre-filtered (0.45 µm filters) water samples were analyzed using an in-line SPE-tandem mass-spectrometry (MS/MS) system including an autosampler and an LC-Pump.

6.2.2.3 Fish, sediment, sludge and soil sample clean-up

The solid samples were freeze dried and thawed prior to extraction. They were extracted using a soxhlet apparatus using methanol as the solvent. The extracts were spiked with labelled simazine as IS and concentrated using a Rotavapor (Büchi, Switzerland). Subsamples of ca 10 µl were analysed on the LC-MS system.

6.2.2.4 LC(/LC)-MS/MS analysis

The LC-MS system includes in-line SPE and a tandem mass-spectrometer (MS/MS) and is equipped with a PAL HTC autosampler (CTC Analytics AG, Zwingen, Switzerland), a Surveyor LC-Pump (Thermo Fisher Scientific, San Jose, CA, USA) connected to a Hypersil GOLD column (20 mm×2.1 mm i.d. x 12 µm particles; Thermo Fisher Scientific) and an Accela LC pump (Thermo Fisher Scientific) with a C18 phase Hypersil GOLD (50 mm x 2.1 mm ID x 3 µm particles; Thermo Fisher Scientific) preceded by a guard column (2 mm×2.1 mm i.d, 3 µm particles) of the same packing material and from the same manufacturer as the analytical column.

Water samples (1 ml) were loaded on the Hypersil GOLD in-line SPE column, used as extraction column, at a flow rate of 1.5 ml min⁻¹. Analytes were eluted off the extraction column and onto the Hypersil GOLD column by a gradient starting with 80% water and

20 % methanol from 0 min to 1.5 min at 250 $\mu\text{L min}^{-1}$ flow, then the gradient is changed linear to 100% methanol at a 400 $\mu\text{L min}^{-1}$ flow in 10 min. This composition of mobile phase and flow were kept for 1 min and then they were switched to the initial conditions and the analytical column was conditioned for 4 min. Extraction column was cleaned by methanol and reconditioned in water between runs. Total time of cycle of the in-line SPE method was 15 min.

The methanol samples were injected (10 μl) directly onto the analytical column, by-passing the in-line SPE column.

Heated electrospray (HESI) in positive ion mode was used for ionization of benzotriazoles. Key parameters were set as follows: ionization voltage 3.5 kV, sheath gas 50 and auxiliary gas 35 arbitrary units, vaporizer temperature 200°C, capillary temperature 325°C and collision gas (argon) flow 1.5 ml min⁻¹. Two SRM transitions were monitored for both the target compound and the internal surrogate standard simazine (Table 11). Both first and third quadrupoles were operated at resolution 0.7 FMWH. Samples were quantified using the internal standard method with 5 calibration points. The maximum difference between results at quantification and qualification mass transition was set to 20% as criterion for positive identification. The data processing and instrument (LC/LC-MS/MS) control were performed by the Xcalibur software.

Table 11: Molecular ion, major fragments and limit of detection for benzotriazoles

Compound	Parent ion {M+H} ⁺	Daughter ions Quan/Qual	Limit of detection
UV328	352.2	282.2/212.1	*
UV329	324.2	212.2/92.2	*
UV320	324.2	268.2/212.2	*
UV327	358.1	302.2/246.2	*
UV234	448.2	370.3/119.2	*
UV P	226.1	77.6/120.2	*
UV360	659.4	336.3/265.1	*

* Specified for each sample in Appendix 2. Based on the lowest calibration solution detected.

7 Results

The results from the measurements of benzothiazoles, benzenediamines, dicyclohexylamine and benzotriazoles are presented in detail in Appendix 2 where the concentrations of the individual substances are given.

7.1 Benzothiazoles, benzenediamines, dicyclohexylamine

7.1.1 Method development

The development of a novel analytical method to determine a variety of benzothiazoles, aromatic amines and cyclic amines in environmentally relevant matrices posed a great challenge due to large differences in physical and chemical properties between the selected substances. For instance, secondary amines, present in five of the eight selected compounds (Table 1), can become protonated and positively charged at $\text{pH} < 9$. The positive charge makes them electrostatically interact with solid surfaces, since the net surface charge of solid surfaces often is negative. Therefore, an extensive set of solvents, with and without acetic acid buffer, was investigated in an attempt to recover compounds with secondary amines from pre-spiked solid matrices. Despite the effort, the experiment revealed generally rather low recovery of compounds with secondary amines from solid matrices. The finding indicates that compounds containing secondary amines in environmental solid matrices predominantly will be present in its bound form.

In summary, two of the substances DCHA and MBT were quantified in all matrices with high recovery. CBS and DBS were quantified with high recovery in abiotic matrices, water and sediment/soil/sludge, while the recovery in biota was low. DBD and DPP were only quantified in abiotic matrices. However, the recovery of DBD and DPP in sediment/soil/sludge was low. TBS and BBD were not possible to analyse at all.

7.1.2 Detection frequencies

An overview of the detection frequencies, *e.g.* the fraction of samples where a substance was found in a concentration above the detection limit for the different sample matrices is given in Table . As mentioned above some of the substances showed low recoveries or were not possible to analyse in some matrices which is important to consider in the evaluation of the results.

Table 12: Detection frequency (%) of the individual benzothiazoles, benzenediamines and dicyclohexylamine for the different sample matrices (Atm. dep= atmospheric deposition; sed=sediment). Detection frequencies of 100 % are marked in dark blue and all other frequencies >0 are marked in light blue, no recovery are marked with -.

Matrix	Air	Atm. Dep.	Surface water	Sed.	Crops	Soil	Biota	Storm water	Effluent, landfill	Effluent, WWTP	Sludge, WWTP
No of samples:	8	4	11	6	4	6	19	4	2	5	5
	%	%	%	%	%	%	%	%	%	%	%
Benzothiazoles											
MBT, Benzothiazole-2-thiol	0	0	36	0	0	0	74	50	100	80	100
CBS, N-cyclohexyl-benzothiazole-2-sulphenamid,	0	0	0	0	0	0	100	0	0	0	0
DBS, N,N-dicyclohexylbenzothiazole-2-sulphenamid,	0	25	0	0	0	0	0	0	100	0	0
DBD, Di(benzothiazol-2-yl) disulphide,	0	0	0	33	-	17	-	0	0	0	0
Benzenediamines											
DPP, N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine,	0	25	27	0	-	0	-	25	0	0	20
DCHA, Dicyclohexylamine,	100	100	45	33	0	67	26	75	100	100	100

DCHA was the most frequently detected substance and it occurred in all sample types except crops. MBT was the benzothiazole with the highest detection frequency. It occurred in most of the samples from WWTPs and landfills. It was also detected in surface water and in different biota samples. CBS was detected in all biota samples but not in any of the other sample matrices. However the analytical recovery of CBS in biota was low. DBS was found in the landfill effluents and in one of the deposition samples. DBD was not found in water but occasionally in sediment and soil. The benzenediamine DPP was occasionally detected in some of the matrices. In the following, the results will be presented in more detail.

7.1.3 Air and deposition

The atmospheric concentrations of DCHA at background, urban and industrial sites are shown in Figure 7. DCHA was the only screened substance that was found in air and it occurred in all samples. The concentrations in urban air in Stockholm and Borås varied between 4.1 and 29 $\mu\text{g}/\text{m}^3$, which were in the same level as in background air (15 $\mu\text{g}/\text{m}^3$ at Råö on both sampling occasions). The highest concentrations were measured in the industrial area Stenungsund (30 and 82 $\mu\text{g}/\text{m}^3$).

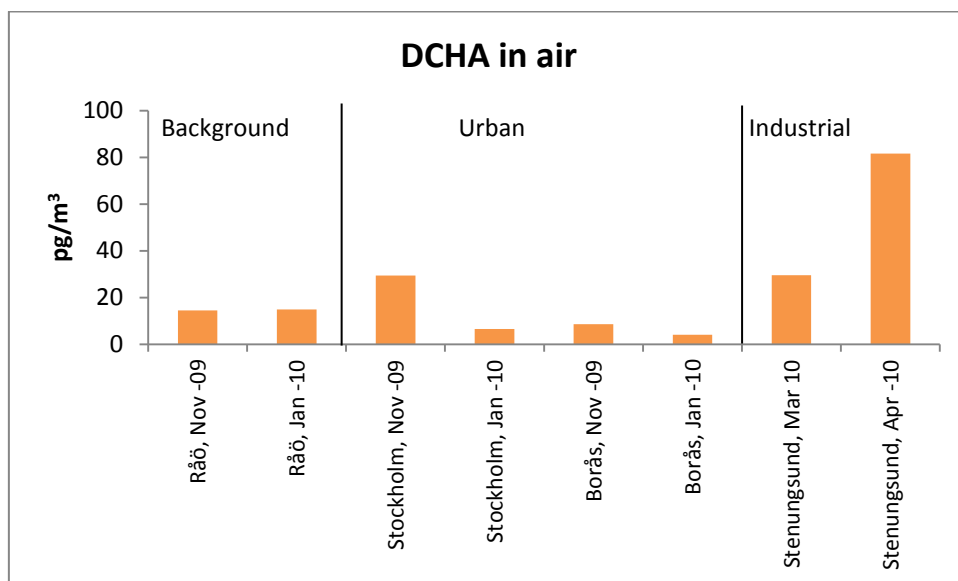


Figure 7 Concentrations of DCHA in air

Atmospheric deposition of DCHA occurred during all sampling occasions, both at background and in urban areas, but there was a variation in the deposition rate of DCHA among the different sampling occasions, see Figure 8. The highest deposition flux, 800 ng/m² day occurred during January 2010 at Valhallavägen, a busy road in Stockholm.

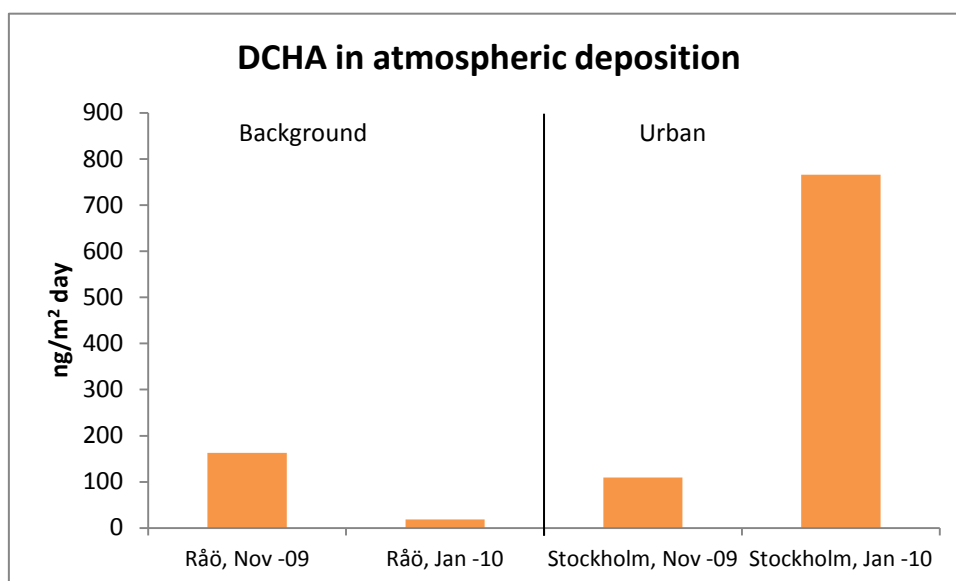


Figure 8 Deposition fluxes, daily averages, of DCHA at background- and urban sites

Deposition of the benzothiazole DBS (53 ng/m² day), was measured at one sampling occasion in Stockholm, November 2010, when also deposition of the benzenediamine DPP (480 ng/m² day) occurred. However due to low analytical recovery these results should be taken only as an indication of a possible pathway for these substances.

Woldegiorgis *et al.* (2008) measured atmospheric concentrations of DCHA which were lower or similar in comparison to the present study. Remberget *et al.* (2006) measured MBT in air and deposition. They did not detect the substance in air but found deposition fluxes between <5 and $37 \text{ ng/m}^2 \text{ day}$, which is higher than found in the present study ($<0.3 \text{ ng/m}^2 \text{ day}$), see Table 3.

7.1.4 Soil and plants

DCHA was detected in soil both in central Stockholm and close to a busy highway. The concentration of DCHA in the two soil samples from central Stockholm were 0.17 ng/g DW and 2 ng/g DW and the concentration 10 m from the road was 3.3 ng/g DW , see Figure 9. The DCHA concentration in soil from the background site was below the detection limit ($<0.2 \text{ ng/g DW}$).

DCHA was not found in crops (wheat) collected in a gradient from a busy road. Thus no uptake of DCHA in these crops was observed.

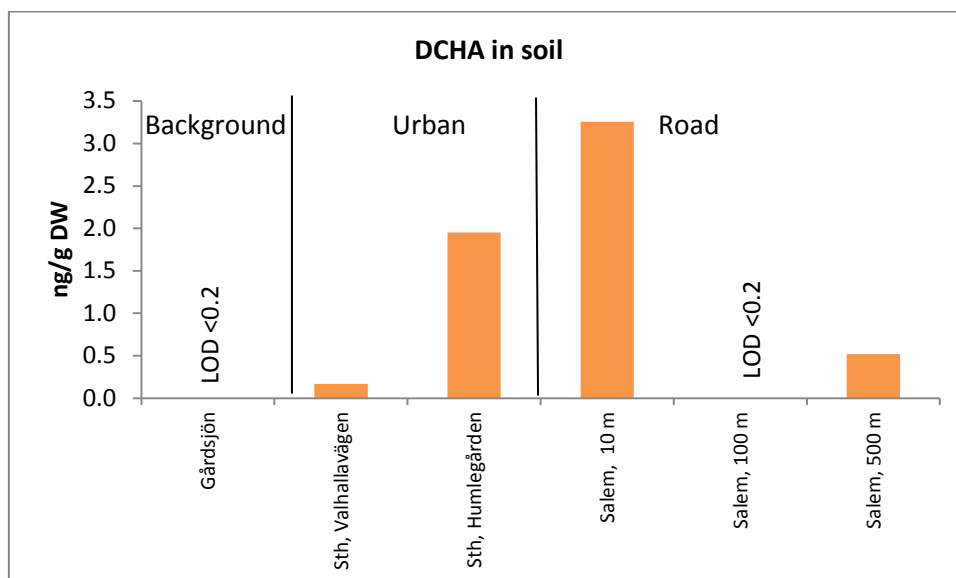


Figure 9 Dicyclohexylamine (DCHA) concentrations in soil. The samples at Salem were collected with increasing distance to the road.

Woldegiorgis *et al.* (2008) measured DCHA in soil at urban and background locations and found concentrations approximately one order of magnitude higher compared to these results (see Table 3).

Except for DBD which was detected in soil from the Gårdsjön area (30 ng/g DW) none of the other substances was found neither in soil nor in crops.

7.1.5 Surface water

Three of the substances were detected in surface water (MBT, DPP, DCHA). The concentrations of DCHA in surface water varied between <2 ng/L and 49 ng/L and of MBT between <3 ng/L and 19 ng/L. DCHA was not detected in the surface water from any of the background lakes while MBT was found in Lake Gårdsjön (see Figure 10).

The highest water concentration of DCHA and MBT were detected in River Viskan, both upstream and downstream Gässlösa WWTP. Both these substances were also found in the surface water collected outside Stenungsund while only DCHA occurred in the water samples from Stockholm.

The only other substance found in surface water was the benzenediamine DPP which occurred in River Viskan. The concentrations were similar (190 and 180 ng/L) upstream and downstream Gässlösa WWTP.

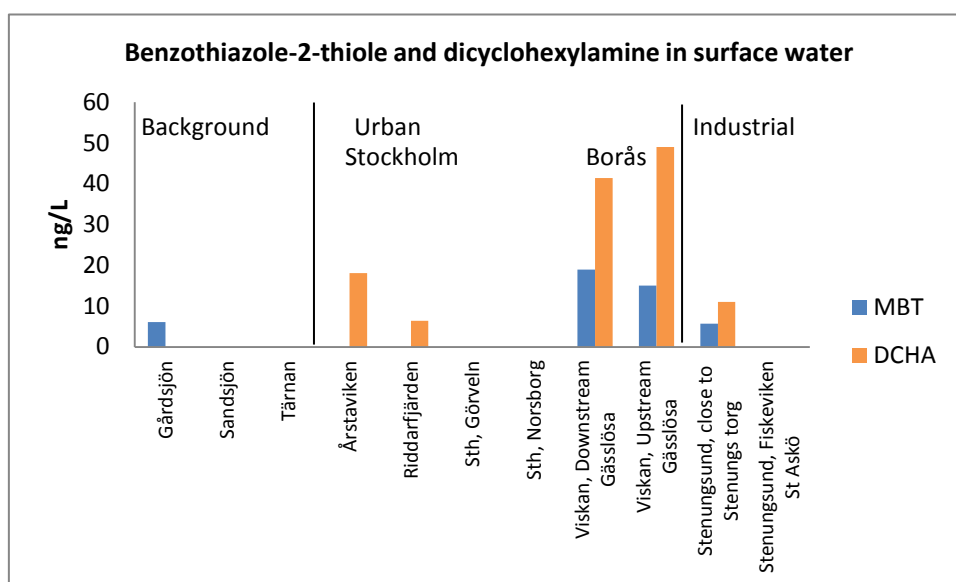


Figure 10 Concentration of Benzothiazole-2-thiole (MBT) and dicyclohexylamine (DCHA) in surface water.

Remberger *et al.* (2006) measured MBT in surface water in concentrations <50-80 ng/L, which is higher than the concentrations found in the present study. Woldegiorgis *et al.* (2008), on the other hand, measured DCHA in surface water in concentrations lower in comparison to the results in the present study. See Table 3.

7.1.6 Sediment

Only one of the benzothiazoles, DBD, was occasionally detected in sediment and surprisingly in two of the background samples where the concentrations were 3.8 and 31 ng/g DW. The levels of the other benzothiazoles, MBT, CBS and DPP in sediment were below the detection limit <1 ng/g DW. The benzenediamine DPP was not detected in sediments (<0.6 ng/g DW).

DCHA occurred in two of three sediment samples from the Stockholm area (0.37 and 0.77 ng/g DW). The concentration in samples collected at background sites were below the detection limit (0.2 ng/g DW).

In comparison Remberger *et al.* (2006) found MBT in sediment samples, in concentrations up to 70 ng/g DW and Kumata *et al.* (2000; 2002) found CBS in concentrations 2.3-17 ng/g DW in river sediments in Tokyo. Woldegiorgis *et al.* (2008) studied the occurrence of DCHA in sediments and found concentrations between <2.3-3.6 ng/g DW, which is higher compared to the findings in the present study. See Table 3.

7.1.7 Biota

The biota samples from the aquatic environment included blue mussels from the Swedish west coast and fish, mainly perch, which were collected in background lakes and in the Stockholm area. Two of the benzothiazoles, CBS (100%) and MBT (75%), and DCHA (26%) were found in the biota samples while the other substances did not occur at all (see Table).

The blue mussels were collected at background sites and at two possibly affected areas, the industrial area Stenungsund and the vicinity to Lysekil where an oil refinery is located. The concentrations of CBS, MBT and DCHA found in the blue mussels are shown in Figure 11 - Figure 13.

CBS was found both in mussels from background sites and from the potentially affected areas in concentrations between 130 and 1000 ng/g DW. The highest concentration occurred in one of the samples from the Lysekil area, otherwise the concentrations in mussels from background sites were mostly higher or in the same levels that in mussels from potential affected sites. However, the analytical recovery of CBS in biota was low and major conclusions about differences in concentrations among different sample locations should not be drawn.

The concentration of MBT varied between <5 and 59 ng/g DW. The substance was detected in one of the background samples in the same level as in mussels from the potentially affect areas. One of the samples from Lysekil contained an increased concentration compared to the other samples. The highest concentration of MBT coincided with the highest concentration of both CBS and DCHA.

DCHA was occasionally found in the mussels both from background- and affected sites. The concentration of DCHA in the mussels from Hamrevik was 18 ng/g DW while the concentrations in the other samples varied between < 1 and 5.4 ng/g DW.

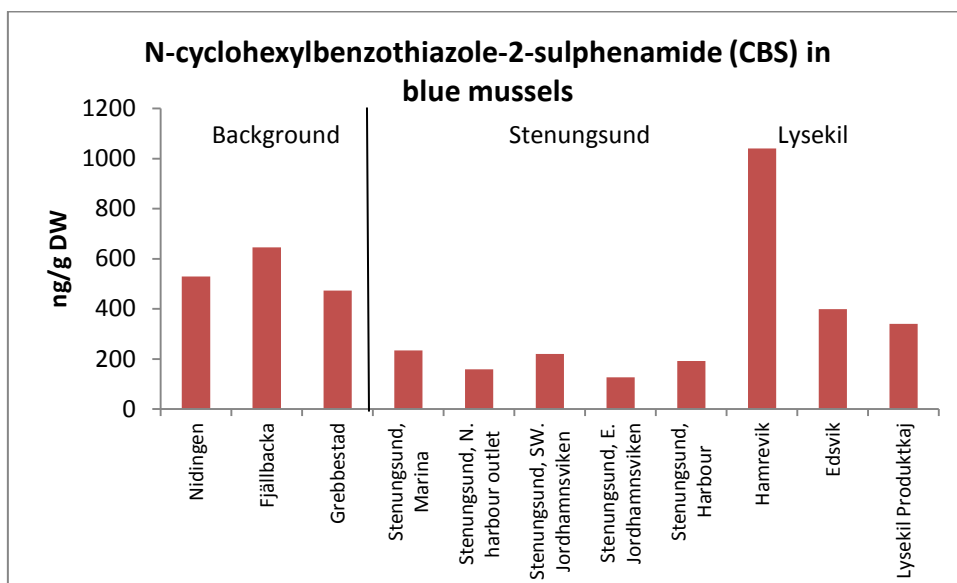


Figure 11 Concentration of N-cyclohexylbenzothiazole-2-sulphenamid (CBS) in blue mussels.

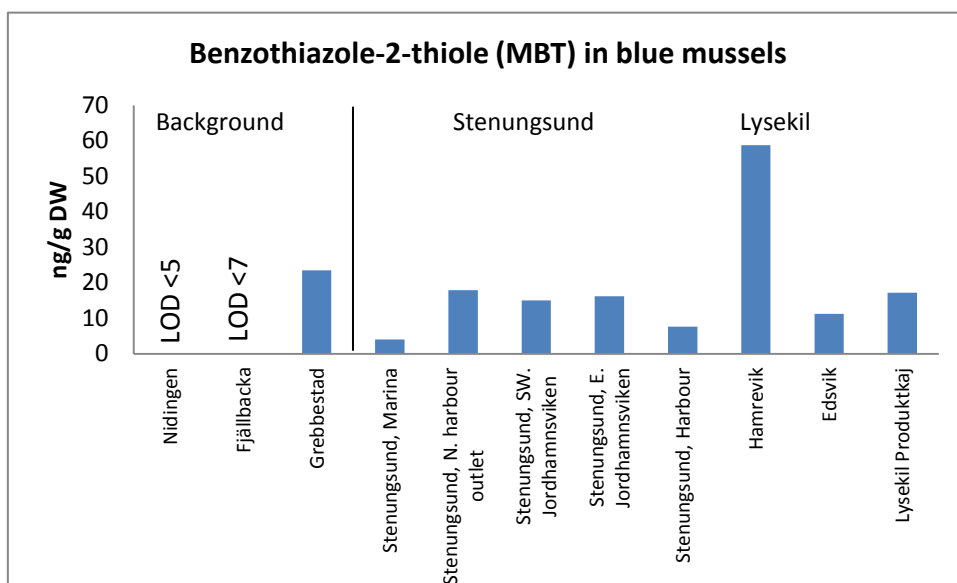


Figure 12 Concentration of benzothiazole-2-thiole (MBT) in blue mussels.

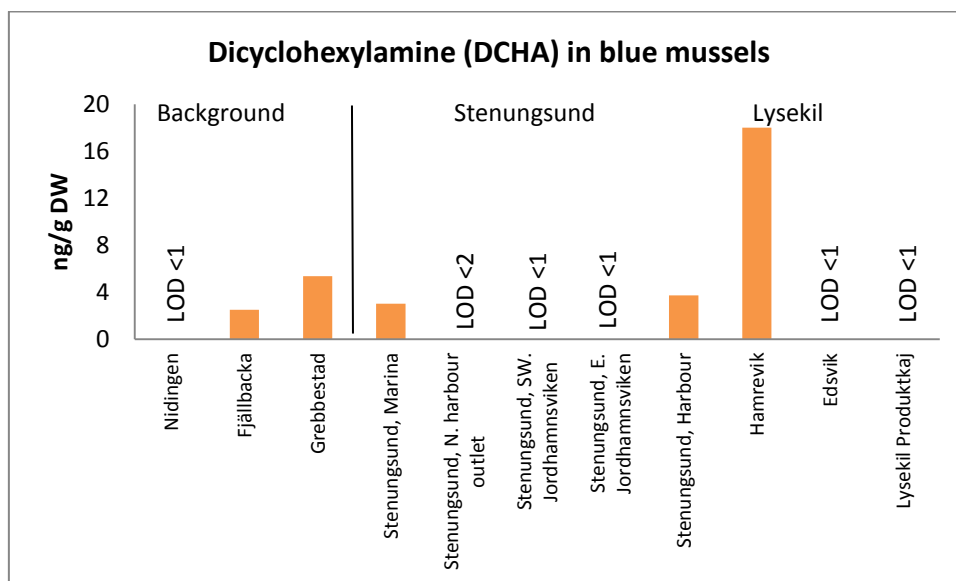


Figure 13 Concentration of dicyclohexylamine (DCHA) in blue mussels.

The two benzothiazoles CBS and MBT, were detected also in fish from background lakes and in fish collected at different sites in the Stockholm area. CBS were found in all eight samples in concentration between 5 and 12 ng/g DW while MBT occurred in five out of eight samples in concentration of 4.5-7.4 ng/g DW. There were no increased levels in the urban influenced samples compared to the background samples. DCHA was not detected in any of the fish samples (<0.5 ng/g DW).

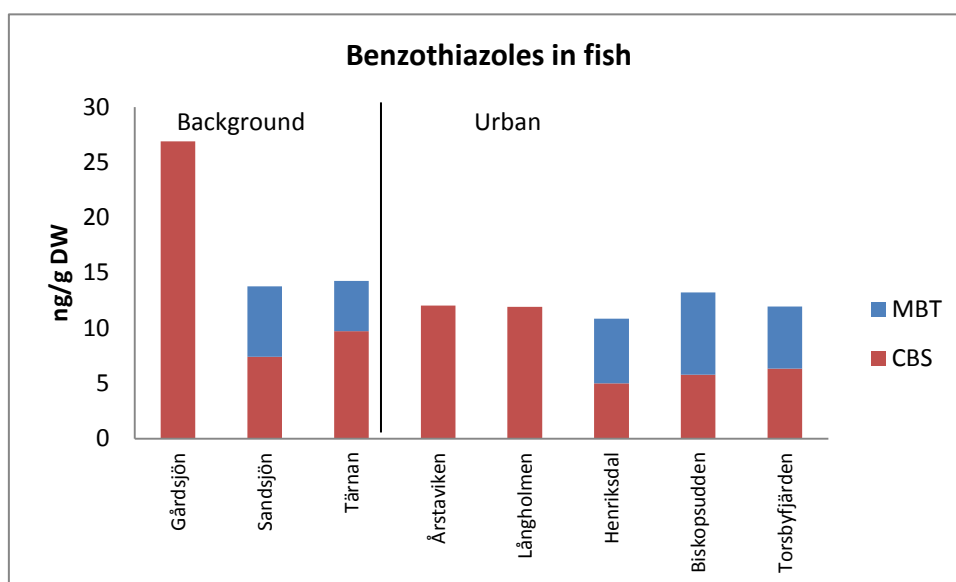


Figure 14 Concentration of Benzothiazole-2-thiole (MBT) and N-cyclohexylbenzothiazole-2-sulphenamide (CBS) in fish.

Few results from previous studies of these substances were found in the literature; Remberger *et al.* (2006) studied the occurrence of MBT in fish but could not detect the substance (<10 ng/g WW). As the detection level was lower in the present study comparisons are difficult.

7.1.8 Waste water treatment plants (WWTPs)

The benzothiazole MBT and dicyclohexylamine (DCHA) were frequently detected both in effluent water and sludge from WWTPs, see Figure 15 and Figure 16. In the figures the WWTPs are arranged from south to north and the relation to person equivalents is also shown.

Five WWTP effluents were analysed. MBT was found in four (<6 - 59 ng/L) and DCHA in all five (42 - 230 ng/L). DCHA occurred mostly in higher concentrations than MBT, highest in samples from the most populated areas Göteborg (Ryaverken) and Stockholm (Käppala and Henriksdal). None of the other substances were detected in the WWTP effluents.

Both MBT and DCHA occurred in all five WWTP sludge samples (10 - 22 ng/g DW and 2.1 - 15 ng/g DW respectively). In contrast to the effluent waters, the concentrations of MBT in sludge were mostly higher than those of DCHA. The benzenediamine DPP occurred in one sludge sample (27 ng/g DW).

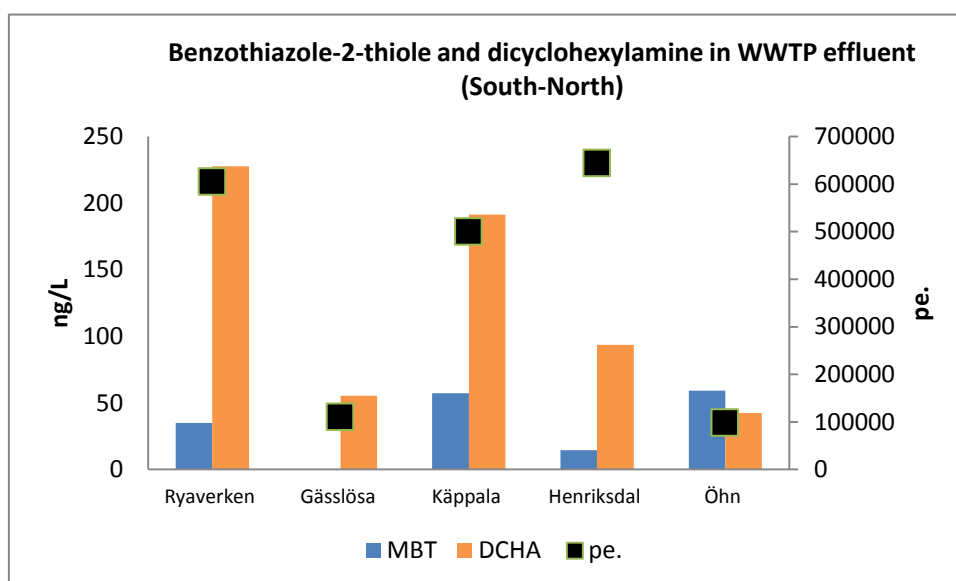


Figure 15 Concentration of benzothiazole-2-thiole (MBT) and dicyclohexylamine (DCHA) in effluent from WWTPs. pe= personal equivalents

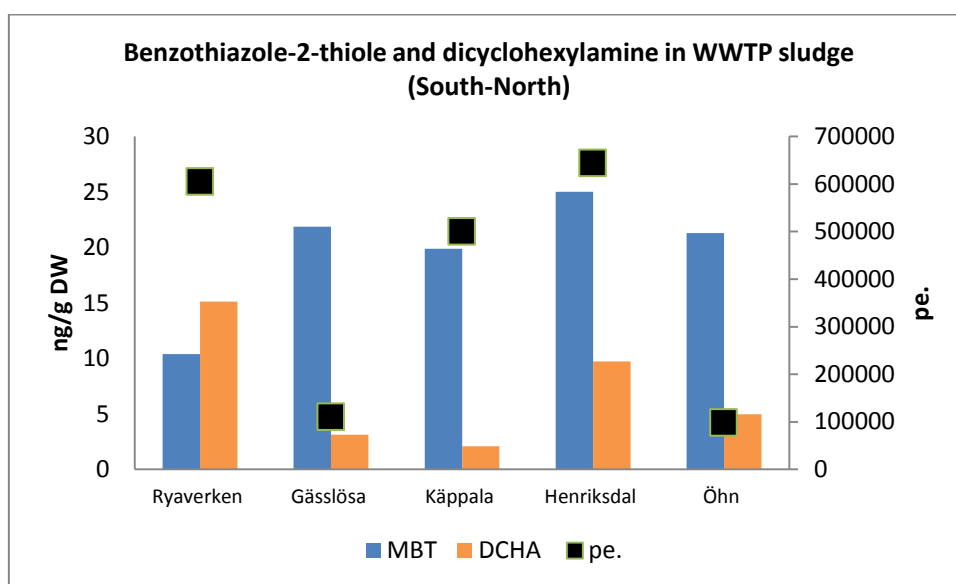


Figure 16 Levels of Benzothiazole-2-thiole (MBT) and dicyclohexylamine (DCHA) in sludge from WWTPs. pe= personal equivalents

Remberger *et al.* (2006) and Kloepfer *et al.* (2005) studied MBT in WWTP effluent and found concentrations <50 - 630 ng/L. In a previous study on DCHA on the other hand, effluent concentrations were lower than those found in the present study (Woldegiorgis *et al.* 2008). See Table 3.

7.1.9 Landfill

Both MBT and DCHA were found in the two leachate samples from landfills in concentrations 84 - 100 ng/L and 36 - 71 ng/L, respectively (Figure 17).

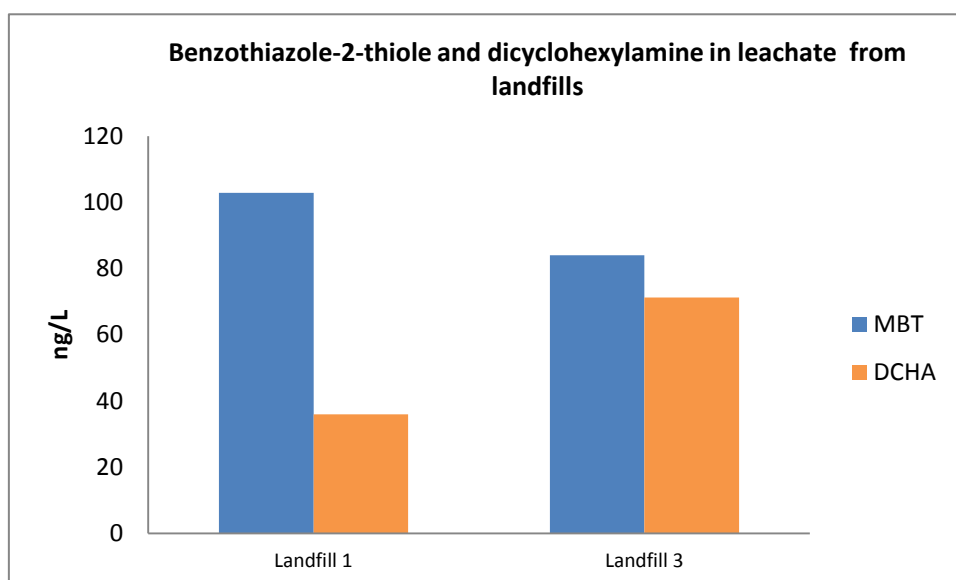


Figure 17 Concentrations of benzothiazole-2-thiole (MBT) and dicyclohexylamine (DCHA) in leachate from landfills. The sample from landfill 2 was only used in analyses of benzotriazoles.

The benzothiazole DBS was also found in the two landfills samples in concentrations 18 and 19 ng/L.

Remberger *et al.* (2006) measured MBT in landfill leachates before and after treatment and after the water had passed an aeration pond and found levels between <50 and 18000 ng/L, with higher concentrations after treatment. Woldegiorgis *et al.* (2008) measured DCHA in landfill leachates and found concentrations <5.4 – 1300 ng/L. For both substances the maximum concentrations were higher than what was found in the present study.

7.1.10 Storm water

MBT and DCHA were detected in storm water both from Stockholm and Borås. The highest concentrations occurred in the sample collected at the bus station in Borås where DCHA and MBT were found in concentrations of 990 and 200 ng/L respectively (Figure 18). DPP was found in one storm water sample (210 ng/L).

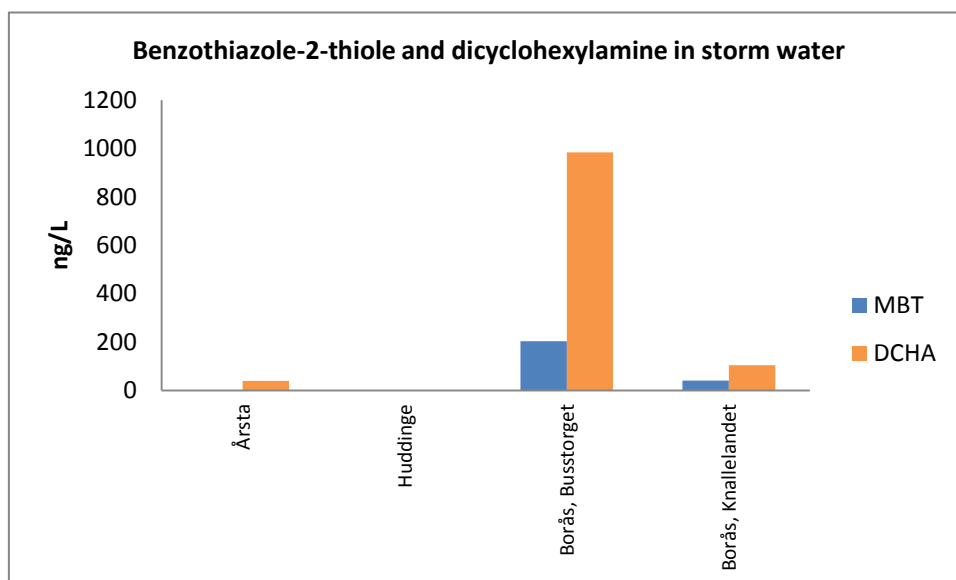


Figure 18 Concentration of Benzothiazole-2-thiole (MBT) and dicyclohexylamine (DCHA) in storm water.

Data from previous studies on occurrence in storm water was only found for DCHA (Table 3). The concentration range found by Woldegiorgis *et al.* (2008), <5.4 - 940 ng/L is similar to the present study (<11 - 990 ng/L).

7.1.11 Toxicity

MBT, DBS, DPP and DCHA were found in water samples; surface water, WWTP effluents, landfill leachates and storm water. To assess the potential risk to the aquatic ecosystem due to the release of these compounds the measured concentration (measured environmental concentration, MEC) was compared to the predicted no effect concentration (PNEC) as found in the literature, see Table).

Table 13 Predicted No Effect Concentration (PNEC) for the aquatic environment (substances in the screening found in water samples).

Substance	PNEC (ng/L)	Reference
MBT	250	Remberger <i>et al.</i> 2006
DBS	No acute or chronic aquatic ecotoxicity within the substance's solubility	Molander 2010
DPP	28	OECD SIDS 2004
DCHA	160	Woldegiorgis <i>et al.</i> 2008

In Table the MEC/PNEC quotients are listed. A MEC/PNEC quotient above 1 indicates that there is a risk of negative effects in the aquatic environment. The maximum concentration of DPP in surface water exceeded the PNEC, the median concentration of all samples did however not; of all samples the PNEC of DPP was exceeded in two. The maximum concentration of DCHA in surface water was relatively close to the PNEC with a MEC/PNEC ratio of 0.31. In the different effluents (WWTP and storm water) maximum concentrations of DPP and DCHA exceeded their respective PNEC.

For the effluents it is relevant to also consider dilution; applying a dilution factor of 10 to the measured concentration means that no maximum concentration would exceed the PNECs and no median concentration would be larger than one tenth of the respective PNEC.

Table 14 Measured concentration (MEC) in relation to predicted no effect concentration (PNEC), *i.e.* MEC/PNEC. These quotients were derived irrespective of dilution in the recipient. Green cells contain values <0.1, yellow 0.1-1 and red ≥ 1 . Not measurable concentrations were set to the detection limit in the calculation of median values. NA= not applicable; concentration were below the reporting limit in all samples.

Substance	Surface water (n=11)	WWTP effluent (n=5)	Landfill leachate (n=2)	Storm water (n=4)
MEC_{max}/PNEC				
MBT	0.076	0.24	0.41	0.81
DBS	No acute or chronic aquatic ecotoxicity within the substance's solubility			
DPP	6.7	NA	NA	7.6
DCHA	0.31	1.4	0.45	6.2
MEC_{median}/PNEC				
MBT	0.024	0.14	0.37	0.095
DBS	No acute or chronic aquatic ecotoxicity within the substance's solubility			
DPP	0.071	0.018	0.018	0.11
DCHA	0.04	0.59	0.34	0.45

DBD was found in soil and sediment and MBT and CBS were found in biota. DCHA was found in soil, sediment, biota and in air. There is thus a possibility that the concentrations found mean that there is a risk of negative effects to soil or sediment dwelling organisms, top predators or other terrestrial animals (including humans). Assessment of such risks

does however require PNECs for these end-points, which was not possible to derive within the scope of the present study.

7.2 Benzotriazoles

7.2.1 Method development

The method development consisted of finding LC-MS conditions suitable for detecting the benzotriazoles chosen. With exception for UV-326 (2-tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol), that couldn't be fragmented and isn't reported, they all gave good product ions for quantification using heated electrospray ionization (HESI) in positive mode (see Table 11).

An overview of the detection frequencies, *i.e.* the fraction of samples where a substance was found in a concentration above the detection limit for the different sample matrices is given in Table .

Table 15 Detection frequency (%) of the individual benzotriazoles for the different sample matrices (Atm. dep= atmospheric deposition; sed=sediment). Detection frequencies of 100 % are marked in dark blue and all other frequencies >0 are marked in light blue.

Matrix	Air	Atm. dep.	Sed.	Biota	Soil	Surface water	Effluent, landfill	Effluent, WWTP	Sludge, WWTP	Storm water
No of samples:	8	4	6	4	4	6	4	6	8	4
UV328	0	0	67	0	25	100	100	100	50	75
UV329	63	75	67	75	75	100	50	100	88	0
UV320	38	0	83	0	25	50	50	17	75	25
UV327	75	75	100	75	75	67	75	83	88	75
UV234	0	0	0	25	0	0	50	17	100	75
UV P	100	50	33	25	50	50	25	33	100	100
UV360	13	0	50	0	0	17	0	0	100	50

In general benzotriazoles were frequently found, the overview indicates a widespread occurrence of these chemicals in the environment and that diffuse spreading through WWTPs, landfills and storm water may be important. Also atmospheric transport and deposition seem to be an important pathway for some of the benzotriazoles.

7.2.2 Air and deposition

In air, the benzotriazole UV P was detected at all sampling occasions and UV327 in 75% of the samples (Figure 19). These substances were also found in the highest concentrations; 0.07-11 ng/m³ and <0.01-25 ng/m³ for UVP and UV327 respectively. UV 329 and UV 320 were found less frequently and in lower concentrations, <0.15-3.0 and <0.03-0.7 ng/m³ respectively. UV 360 was only found at one occasion in a concentration of 0.40 ng/m³. UV

328 and UV 234 were not detected in air. The concentrations were similar in background and urban air although the highest concentration was measured in Stockholm.

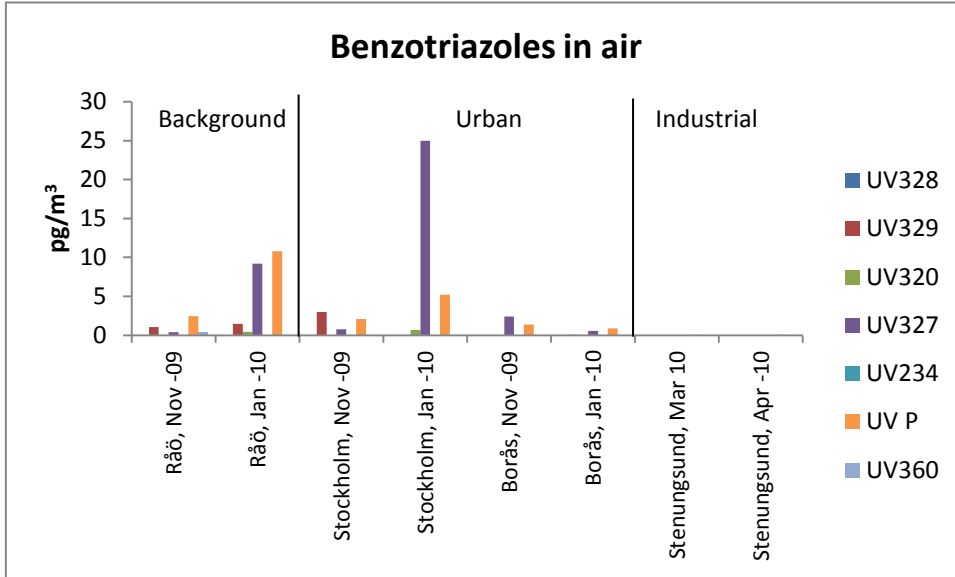


Figure 19 Concentration of benzotriazoles in air from background and urban sites (the abbreviations are explained in Table 1)

In atmospheric deposition only UV 329, UV 327 and UV P were detected. The deposition fluxes were <100-330, <100-320 and <30-860 ng/m² day, respectively (Figure 20). Deposition occurred more frequently in the urban environment compared to background locations. The highest deposition flux was also measured at the urban location.

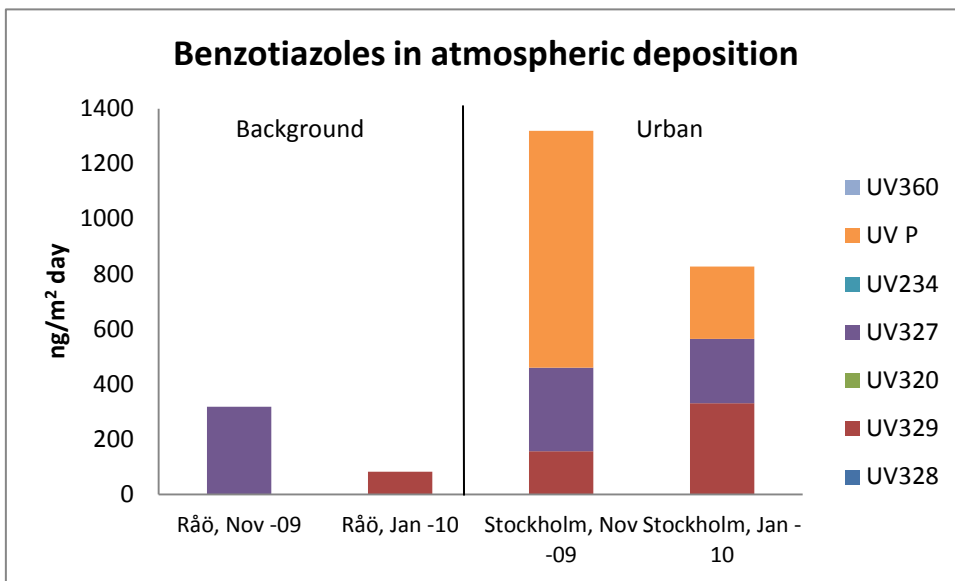


Figure 20 Deposition fluxes of benzotriazoles (the abbreviations are explained in Table 1)

7.2.3 Soil

Several of the benzotriazoles were found in soil, in rather similar concentrations at the background and the urban locations (Figure 21). There were however differences in the occurrence among the individual substances at the different locations. The highest concentration of a single substance (UV 329) was found in the soil 500 m from a busy road in the Stockholm area (Salem); 3.7 µg/g DW. UV 360 and UV 340 were not detected in soil.

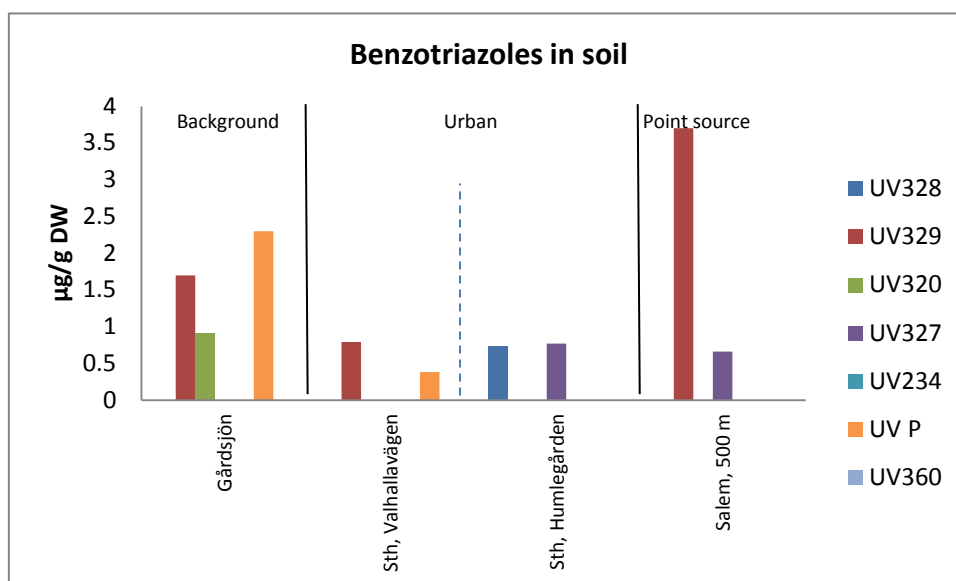


Figure 21 Benzotriazoles in soil samples (the abbreviations are explained in Table 1)

7.2.4 Surface water

Several of the benzotriazoles were frequently detected in surface water. UV328 and UV 329 were found in all samples in the concentration range 1.7 – 10 ng/L and 0.25-2.4 ng/L, respectively. The concentrations were mostly similar at background and urban locations (Figure 22).

Increased concentrations of UVP were measured in River Viskan both upstream and downstream the WWTP Gässlösa (22 respective 18 ng/L) and in one of the samples from Stockholm (Riddarfjärden, 15 ng/L). The concentrations of UVP in the background lakes were below the detection limit (<0.1 ng/L), Figure 23. UV P was found in the same levels in effluent water as in surface water, see below.

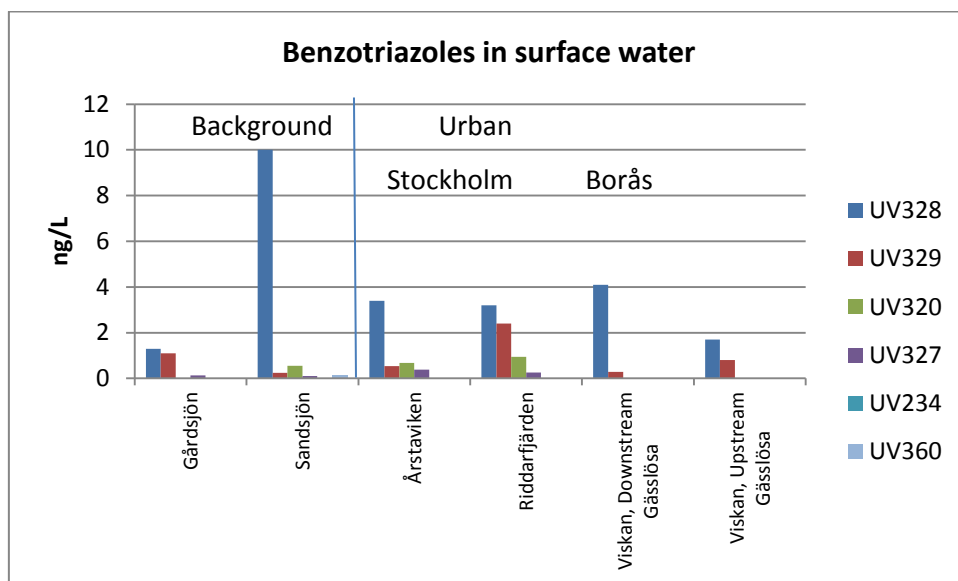


Figure 22 Concentration of detected benzotriazoles, except UV P, in surface water (the abbreviations are explained in Table 1)

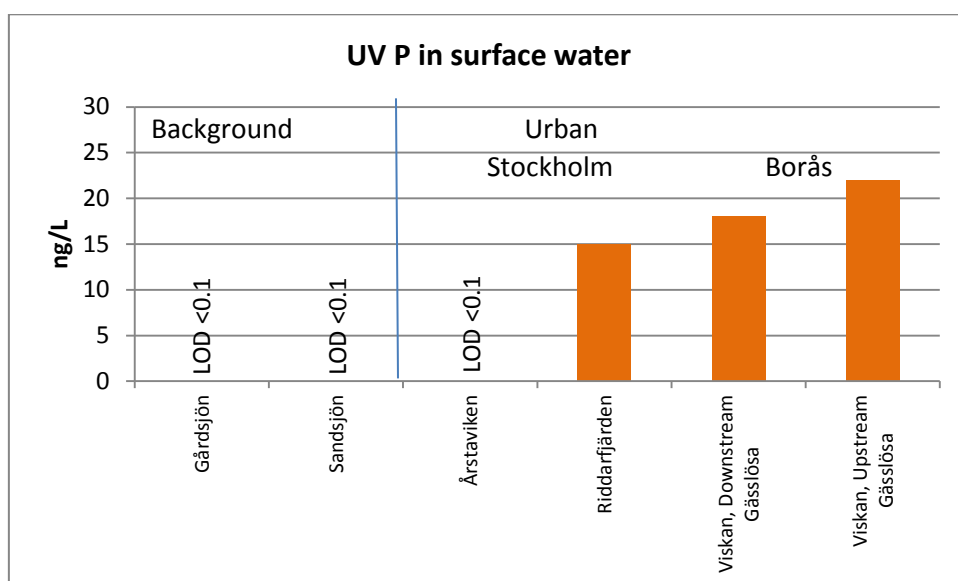


Figure 23 Concentration of 2-(benzotriazol-2-yl)-4-methylphenol (UV P) in surface water

7.2.5 Sediments

In sediments all substances (except UV 234) were found in concentrations between 0.16 and 35 µg/g DW. The distribution among different substances varied for the different sampling sites (Figure 24). Peaks of single substances occurred both at background and urban locations; the lower concentration levels were similar at different locations.

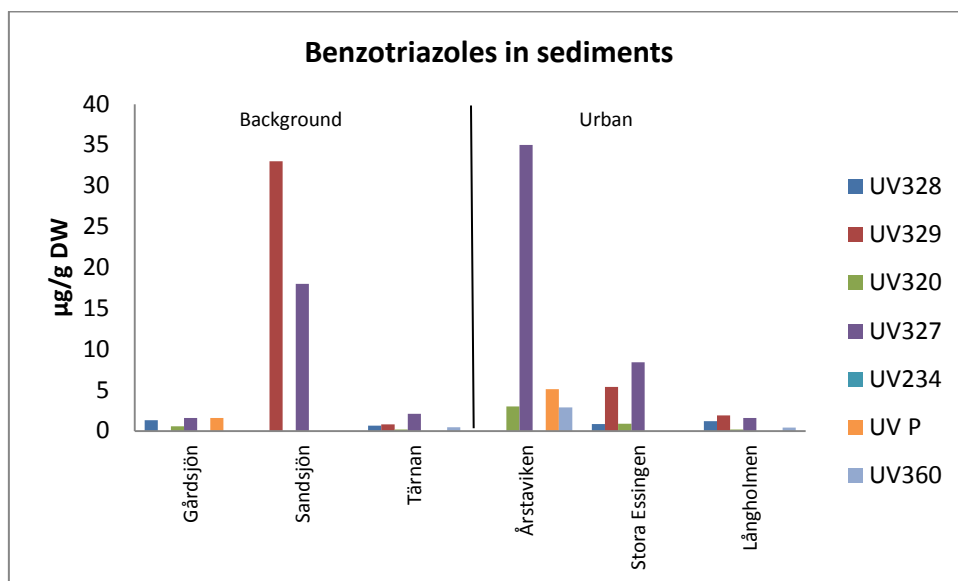


Figure 24 Concentration of benzotriazoles in sediments from background and urban sites (the abbreviations are explained in Table 1)

7.2.6 Biota

UV 329 and UV 327 were detected in three out of four fish samples, both at urban and background locations; the highest concentration was found at the background location Lake Gårdsjön (UV 327, 9.8 µg/g DW). Also UV 234 and UV P were found, but only in one out of four samples. See Figure 25.

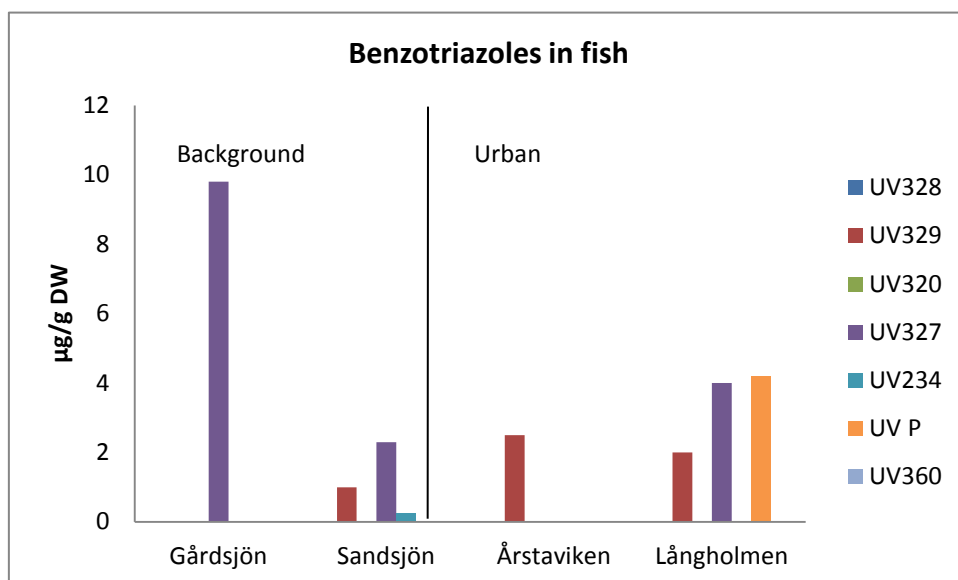


Figure 25 Concentration of benzotriazoles in fish from background and urban sites (the abbreviations are explained in Table 1)

7.2.7 WWTP effluent and sludge

The benzotriazoles were frequently detected both in effluent water and in sludge from WWTPs. However there were differences both in concentration levels and in distribution among the different benzotriazoles between the WWTPs. A different distribution among the substances was also found between the effluent and sludge; see Figure 26 and Figure 27. The WWTPs are arranged from south to north and the relation to person equivalents is also shown.

The total concentration of the benzotriazoles in the effluents varied between 12 and 49 ng/L. UV328 and UV329 (6.8-15 and 0.87-4.9 ng/L respectively), were the most common substances in the effluents while UVP (<0.1-33 ng/L) occurred in the highest concentration in the effluent from Öhn WWTP (Umeå).

Most of the benzotriazoles were found in sludge. The total concentration varied between 34 and 82 ng/g DW. UV 328, UV 329 and UVP occurred in the highest concentrations (<0.1-37, <0.2-28 and 6.9-18 µg/g DW respectively).

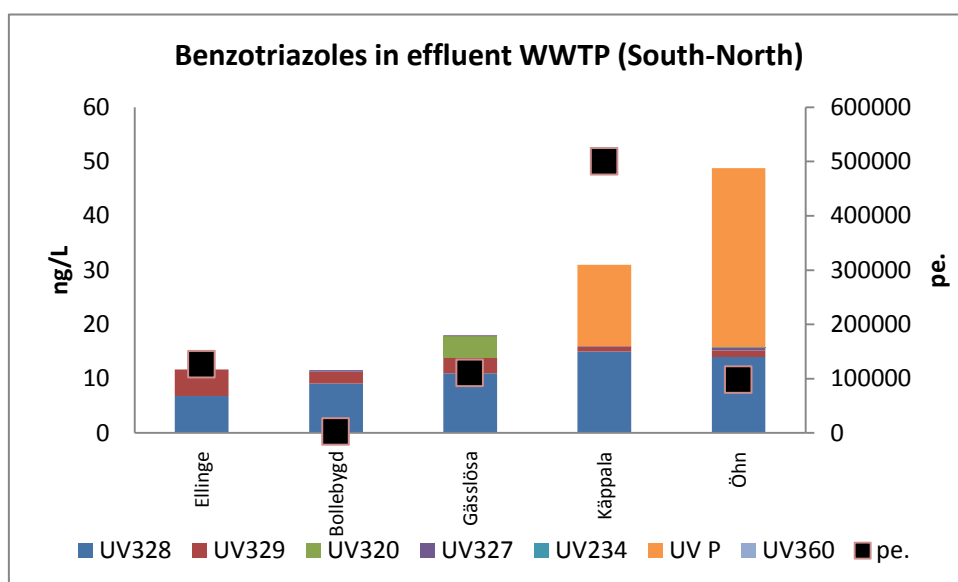


Figure 26 Concentration of benzotriazoles in effluent from WWTPs (the abbreviations are explained in Table 1)

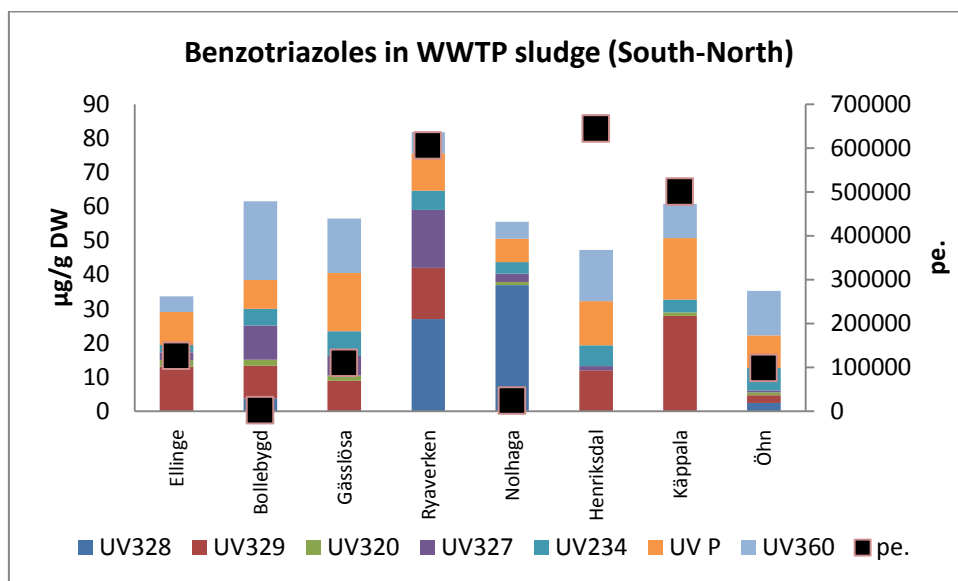


Figure 27 Concentrations of benzotriazoles in sludge from WWTPs (the abbreviations are explained in Table 1)

7.2.8 Landfills

UV 328 was found in all three landfill leachates and also in the highest concentrations (7.0-91 ng/L). UV 320 (7.3 and 23 ng/L) and UV 234 (0.16 and 0.5 ng/L) were found in two out of three samples while UV 329 and UV 327 were found in one sample each (17 and 1.3 ng/L, respectively).

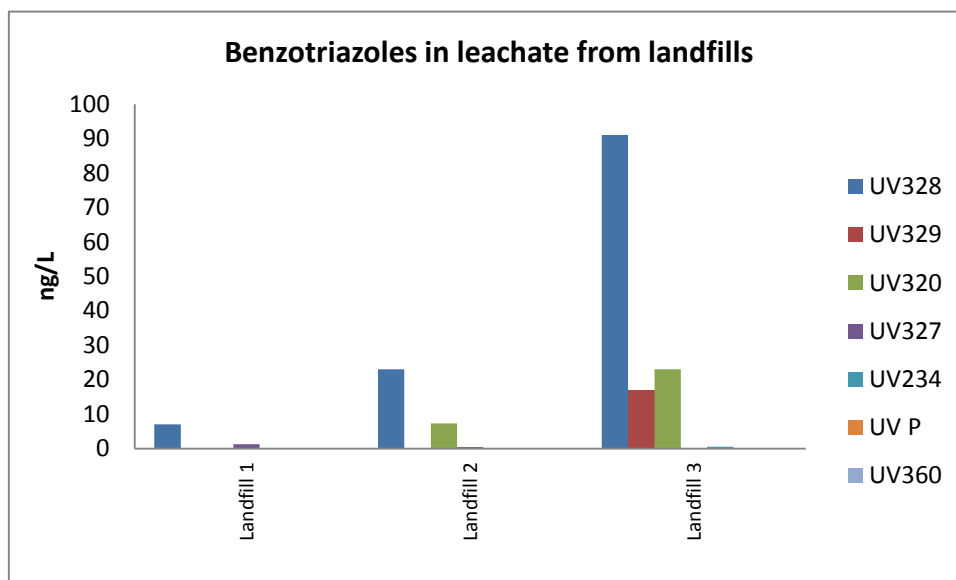


Figure 28 Concentrations of benzotriazoles in leachate from landfills (the abbreviations are explained in Table 1)

7.2.9 Storm water

UVP was the dominating benzotriazole in storm water and occurred in concentrations between 1.1 and 10 ng/L. Several of the other benzotriazoles were also detected but in lower concentrations (Figure 29 and Figure 30).

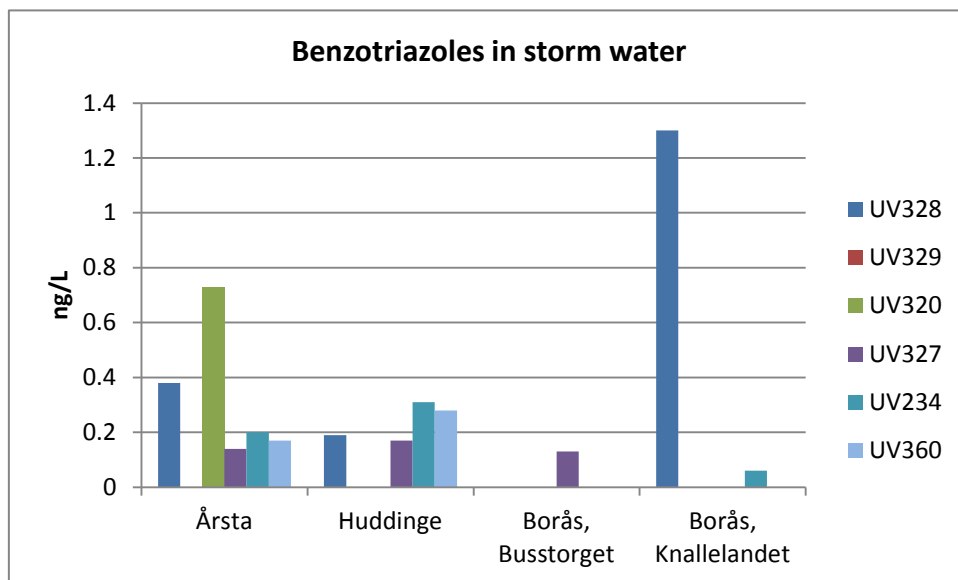


Figure 29 Concentration of benzotriazoles in storm water (the abbreviations are explained in Table 1)

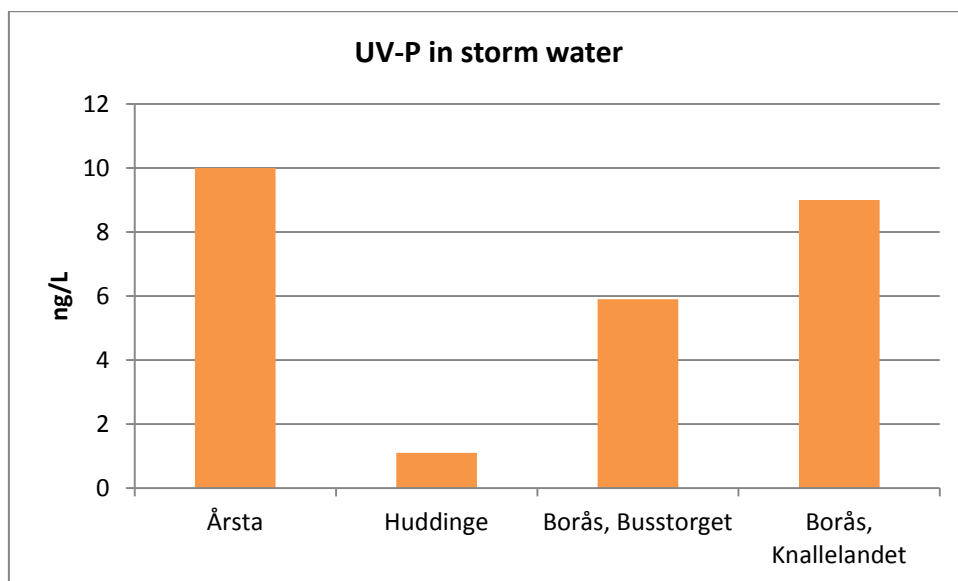


Figure 30 Concentration of UV-P in storm water

8 Summary and conclusions

8.1 Benzothiazoles

The benzothiazoles MBT, CBS, DBS and DBD were found in one or more of the sample matrices. TBS was not possible to analyse. The detection frequencies varied both among the substances and the different media. The distribution pattern was most likely affected both by substance properties, *i.e.* the chemical stability and the tendency of a substance to partition to a certain media, and the use and emission pattern. MBT had the highest detection frequency while the other benzothiazoles were more occasionally found.

MBT was not found in air or atmospheric deposition.

MBT was frequently found in WWTP effluents and in sludge. Variations between the plants did however not follow any obvious pattern.

MBT was also found in leachate from landfills and in storm water samples but not in soil or sediment.

MBT was found in surface waters predominantly at urban and industrial locations. The highest concentrations occurred in River Viskan; both upstream and downstream the WWTP which indicates even other sources for the occurrence of this substance in surface waters.

MBT occurred in different aquatic biota samples. The highest concentration was found in mussels collected in the vicinity of an oil refinery. The concentrations in the mussels from the background sites and from potentially affected areas (Stenungsund and Lysekil) were in the same range. MBT was also found in fish samples; where concentrations were in the same range in background and urban samples.

CBS was only found in biota. However, the analytical recovery for this substance was low and the concentrations should be seen only as an indication of the occurrence.

DBD was found only in soil and sediment, it was however not possible to analyse in crops and biota.

An important pathway of MBT to the environment is via WWTPs, an indication that the occurrence is due to diffuse emission from *e.g.* consumer products. The occurrence in storm water indicates traffic related emissions. MBT and the other benzothiazoles did mainly occur in the aquatic environment. Air transport seems to be of minor importance.

8.2 Benzenediamines

The benzenediamine DPP was occasionally detected in some of the matrices e.g. surface water, storm water and sludge. BBD was not possible to analyse.

8.3 Dicyclohexylamine

DCHA was, consistent with the finding in the previous screening (Woldegiorgis *et al.* 2008), widespread in the environment and it occurred in all sample types except crops.

DCHA was found both in air and deposition. The atmospheric concentrations of DCHA were higher at the industrial site compared to both urban and background locations. The concentrations in background air were lower or in the same level compared to measurements 2007 at the same locations.

DCHA was frequently found in WWTP effluents and in sludge. Landfill leachate concentrations of DCHA were similar or lower, compared to those found in WWTP effluents.

DCHA occurred in surface waters from urban and industrial locations. The highest concentrations were measured in River Viskan; both upstream and downstream the WWTP. DCHA was also detected in sediment.

DCHA occurred in mussels but not in any of the fish samples. The highest concentration was measured in the vicinity of an oil refinery but it was also detected in samples from the background locations.

Urban diffuse emissions to air and influence of traffic seem to be important since both urban soil and soil from the vicinity of a road contained DCHA, which is in agreement with findings in the previous screening study. DCHA was found in storm water, occasionally in high concentrations (up to 990 ng/L).

DCHA was like MBT frequently found in WWTP effluents and in sludge. The concentrations of MBT and DCHA did not correlate.

The findings of DCHA in air and deposition indicate that this substance is emitted to air and that atmospheric transport is an important pathway in the environment. The occurrence in storm water as well as in soil indicates that traffic related emissions are important. DCHA was however not found in crops collected in the vicinity to busy roads. Another important pathway for DCHA to the environment is via WWTPs, an indication that the occurrence is due to diffuse emission from *e.g.* consumer products.

8.4 Benzotriazoles

There is a widespread occurrence of benzotriazoles in the environment both at background and urban areas. The substances occurred in all the included environmental matrices, air, deposition, surface water, sediment, soil and biota.

Similar levels of benzotriazoles were found in samples from urban and background areas, which indicate that, on a national scale, air transport may be a significant source of these compounds.

The occurrence in background areas indicates that these substances are stable enough to undergo atmospheric long range transport. Atmospheric transport and deposition seem to be an important pathway for some of the benzotriazoles. The atmospheric concentrations were similar in background and urban areas, while the deposition was higher at the urban site.

The levels of benzotriazoles were generally similar to those of DCHA and MBT. Increased concentrations of UVP were detected in River Viskan that flow through an area with textile industries. The levels upstream and downstream the local WWTP were however similar.

The benzotriazole levels in sediments were in the low $\mu\text{g/g}$ DW range, which is similar to the levels reported for Japanese background sediments.

The benzotriazole levels were rather constant among the investigated WWTP effluents (total concentrations between 10 and 50 ng/L, dissolved in water) and sludge (total concentrations between 30 and 80 $\mu\text{g/g}$ DW) samples, which indicates widespread diffusive sources.

Landfill leachate and storm water contains similar concentrations of benzotriazoles as the WWTP effluents.

The results also showed that diffuse spreading through WWTPs, landfills and storm water may be important for the occurrence in the environment. This indicates that these substances are distributed via use of products. UVP is the benzotriazole with the highest usage volume followed by UV 328 and UV327. These substances were also most often found in the highest concentrations.

The levels of benzotriazoles in fish were in the low $\mu\text{g/g}$ DW range, which are 1000-fold higher than those found in Japanese fish. The reason for this is not known. It should be noted however that most substances are not detected and the levels found are quite close to the detection limit of the method used.

8.5 Toxicity

A screening contains a limited amount of samples from each of the studied matrices which renders toxicity assessment difficult as large uncertainties are introduced. A brief evaluation of toxicity to aquatic pelagic organisms was however made for substance found in water samples (MBT, DBS, DPP and DCHA). When median concentrations found in surface water were compared to the respective PNEC all risk quotients were <0.1 , *i.e.* no risk could be foreseen. Making the same comparison using the maximum concentrations did however result in a risk quotient >1 for DPP and >0.1 for DCHA. If concentrations remain at such levels during prolonged periods this means that there may be a risk for negative effects.

Also the concentrations in the effluents (WWTP, landfill and storm waters) were set in relation to the respective PNEC. Considering a dilution factor of 10 the risk quotient were not >1 , albeit maximum concentrations of DPP and DCHA in storm waters and landfill leachates did result in a risk quotient >0.1 . There may however exist locations where the dilution is not as high and thus, locally, a risk for negative effects.

Besides the risk of negative effects on the aquatic pelagic ecosystem the findings of these substances in soil, sediment, and biota and in air may pose a risk also to other organisms. This was however not assessed further in the present study.

No toxicity or ecotoxicity data has been found for any of the benzotriazole substances in the available literature. Any risk estimates have therefore not been carried out.

In a brief risk assessment for the aquatic pelagic ecosystems no major risks were identified, *i.e.* concentrations were generally below the PNEC in surface water and effluents if dilution was considered. DPP did however occur in concentrations above its PNEC in River Viskan and concentrations of DPP and DCHA in the different effluents did at some occasions exceed the PNEC undiluted.

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Appendix 1 Environmental samples

Sample ID	Umeå ID	Type	Station	Matrix	Date, start	Date, stop	RT90,X	RT90,Y	Specie	Info
MR 8370	3411:27	Background	Råö	Air	2009-11-02	2009-11-30	6369857	1266139		
MR 8364	3411:26	Background	Råö	Air	2010-01-04	2010-02-01	6369857	1266139		
MR 8361	3411:25	Diffuse	Stockholm, Valhallavägen 81	Air	2009-11-12	2009-12-07	6582787	1629024		
MR 8362	3411:24	Diffuse	Stockholm, Valhallavägen 81	Air	2010-01-26	2010-02-16	6582787	1629024		
MR 8404	3411:23	Diffuse	Borås	Air	2009-11-17	2009-12-15	6403138	1329564		
MR 8405	3411:22	Diffuse	Borås	Air	2010-01-12	2010-02-11	6404373	1328878		
MR 8455	3311:56	Point source	Stenungsund	Air	2010-03-16	2010-03-30	6445904	1266060		
MR 8456	3311:57	Point source	Stenungsund	Air	2010-04-06	2010-04-21	6445904	1266060		
MR 8363	3411:19	Background	Råö	Deposition	2009-11-02	2009-11-30	6369857	1266139		
MR 8374	3411:21	Background	Råö	Deposition	2010-01-04	2010-02-01	6369857	1266139		
MR 8415	3411:28	Diffuse	Stockholm, Valhallavägen 81	Deposition	2009-11-05	2009-12-07	6582787	1629024		
MR 8416	3411:29	Diffuse	Stockholm, Valhallavägen 81	Deposition	2010-01-19	2010-02-16	6582787	1629024		
MR 8217	3411:47	Background	Gårdsjön	Surface water	2009-12-18		6443900	1276500		
MR 7953		Background	Sandsjön	Surface water	2009-09-11					
MR 8423		Background	Tärnan	Surface water	2010-04-15		6608704	164490		
MR 7953	3411:46	Background	Sandsjön	Surface water	2009-09-11					
MR 8158	3411:49	Diffuse	Viskan, Downstream Gässlösa	Surface water	2009-11-19		6401995	1328222		
MR 8159	3411:48	Diffuse	Viskan, Upstream Gässlösa	Surface water	2009-11-19		6401966	1328955		
MR 7959	3411:44	Diffuse	Årstaviken	Surface water	2009-09-16					
MR 7967	3411:45	Diffuse	Riddarfjärden	Surface water	2009-09-16					
MR 8027			Stockholm, Görveln	Surface water	2009-10-13					
MR 8028			Stockholm, Norsborg	Surface water	2009-10-13					
MR 8218		Point source	Stenungsund, close to Stenungs torg	Surface water	2009-12-18					
MR 8219		Point source	Stenungsund, Fiskeviken St Askö	Surface water	2009-12-18					
MR 7674	3411:51	Background	Gårdsjön	Sediment	2008-12-12		6443900	1276500		
MR 7954	3411:16	Background	Sandsjön	Sediment	2009-09-11					
MR 8265	3411:11	Background	Tärnan	Sediment	2009-09-18		6608704	164490		
MR 7960	3411:17	Diffuse	Årstaviken	Sediment	2009-09-16					
MR 7962	3411:18	Diffuse	Stora Essingen	Sediment	2009-09-16					
MR 7968	3411:12	Diffuse	Långholmen/Riddarfjärden	Sediment	2009-09-16					

Sample ID	Umeå ID	Type	Station	Matrix	Date, start	Date, stop	RT90,X	RT90,Y	Specie	Info
MR 8875		Point source	Ekerö, 6 m fr road	Crops (wheat)	2010-07-17					20 000 vehicles/day
MR 8876		Point source	Ekerö, 170 m fr road	Crops (wheat)	2010-07-17					20 000 vehicles/day
MR 8877		Point source	Ekerö, 300 m fr road	Crops (wheat)	2010-07-17					20 000 vehicles/day
MR 8878		Point source	Ekerö, 1500 m fr road	Crops (wheat)	2010-07-17					20 000 vehicles/day
MR 8220	3411:55	Background	Gårdsjön	Soil	2009-12-18		6443900	1276500		
MR 8434	3411:54	Urbant	Stockholm, Valhallavägen	Soil	2010-04-19					
MR 8435	3411:53	Urbant	Stockholm, Humlegården	Soil	2010-04-19					
MR 8114		Point source	Salem, amine gradient 10 m	Soil	2009-11-12		6567251	1612700		
MR 8115		Point source	Salem, amine gradient 100 m	Soil	2009-11-12		6567251	1612700		
MR 8116	3411:5	Point source	Salem, amine gradient 500 m	Soil	2009-11-12		6567251	1612700		
MR 8428		Background	Valön Fjällbacka	Blue mussel	2009-10-19					
MR 8429		Background	Nidingen	Blue mussel	2009-10-15					
MR9052		Background	Grebbestad, Lysekil (Preemraf)	Blue mussel	2010		6515996	1236220		
MR 8601		Point source	Stenungsund, marina	Blue mussel	2010-05-18		6445279	1264624		
MR 8602		Point source	Stenungsund, N harbour outlet	Blue mussel	2010-06-14		6446669	1264213		
MR 8603		Point source	Stenungsund, SW Jordhamnsviken	Blue mussel	2010-06-14		6447648	1265026		
MR 8604		Point source	Stenungsund, E Jordhamnsviken	Blue mussel	2010-06-14		6447866	1265451		
MR 8605		Point source	Stenungsund, harbour	Blue mussel	2010-06-21		6445939	1264658		
MR9049		Point source	Hamrevik (Preemraff)	Blue mussel	2010		6478208	1243044		
MR9050		Point source	Edsvik (Preemraff)	Blue mussel	2010		6478876	1242340		
MR9051		Point source	Produktkaj (Preemraff)	Blue mussel	2010		6478320	1244292		
MR 8387	3411:4	Background	Gårdsjön	Fish	2010-03-17		6443900	1276500	Perch	
MR 8414	3411:3	Background	Sandsjön	Fish	2010-04-06				Perch	
MR 8266		Background	Tärnan	Fish	2009-09-18		6608704	164490	Perch	
MR 8388		Background	Gårdsjön	Fish	2010-03-17		6443900	1276500	Sea trout	
MR 7969	3411:1	Diffuse	Årstaviken	Fish	2009-09-16				Perch	
MR 7972	3411:2	Diffuse	Långholmen/Riddarfjärden	Fish	2009-09-16				Perch	
MR 8400		Diffuse	Henriksdal WWTP	Fish	2010-03-31				Perch	
MR 8402		Diffuse	Stockholm, Biskopsudden	Fish	2010-03-31				Perch	
MR 8403		Diffuse	Stockholm, Torsbyfjärden	Fish	2010-03-31				Perch	
MR 8038	3411:32	Diffuse	Årsta	Storm water	2009-10-16					

Sample ID	Umeå ID	Type	Station	Matrix	Date, start	Date, stop	RT90,X	RT90,Y	Specie	Info
MR 8156	3411:33	Diffuse	Borås, Busstorget	Storm water	2009-11-19		6402995	1329365		
MR 8157	3411:34	Diffuse	Borås, Knallelandet	Storm water	2009-11-19		6404373	1328878		
MR 8039	3411:31	Diffuse	Huddinge	Storm water	2009-10-16					
MR 8058	3411:50	Point source	Landfill 1	Effluent landfill	2008-10-31					
MR 8058	3411:36	Point source	Landfill 1	Effluent landfill	2008-10-31					
MR 8054	3411:37	Point source	Landfill 2	Effluent landfill	2009-10-22					
MR 8059	3411:35	Point source	Landfill 3	Effluent landfill	2009-10-30					
MR 8437	3411:52	Diffuse	Henriksdal WWTP	Effluent	2010-01-21					
MR 8004	3411:38	Diffuse	Gässlösa WWTP	Effluent	2009-09-29	2009-09-30				
MR 8006	3411:39	Diffuse	Öhn WWTP	Effluent	2009-09-30	2009-10-01				
MR 8008	3411:40	Diffuse	Bollebygd WWTP	Effluent	2009-09-29	2009-09-30				
MR 8164	3411:42	Diffuse	Käppala WWTP	Effluent	2009-11-19					
MR 8269	3411:43	Diffuse	Ellinge WWTP	Effluent	2010-01-27					
MR 8211		Diffuse	Ryaverken WWTP	Effluent	2009-12-17					
MR 8232		Diffuse	Henriksdal WWTP	Effluent	2010-01-21					
MR 8005	3411:14	Diffuse	Gässlösa WWTP	Sludge	2009-09-30					
MR 8007	3411:9	Diffuse	Öhn WWTP	Sludge	2009-10-01					
MR 8009	3411:8	Diffuse	Bollebygd WWTP	Sludge	2009-09-30					
MR 8119	3411:7	Diffuse	Nolhaga WWTP	Sludge	2009-11-12					
MR 8165	3411:15	Diffuse	Käppala WWTP	Sludge	2009-11-19					
MR 8212	3411:13	Diffuse	Ryaverken WWTP	Sludge	2009-11-13					
MR 8234	3411:10	Diffuse	Henriksdal WWTP	Sludge	2010-01-31					
MR 8270	3411:6	Diffuse	Ellinge WWTP	Sludge	2010-01-27					

Appendix 2 Individual results

Benzothiazoles and benzenediamines, dicyclohexylamine

("*" Not possible to analyze; "-" No recovery)

Sample ID	Station	Matrix	Unit	MBT	TBS	CBS	DBS	DBD	DPP	BBD	DCHA
				Benzo-thiazole-2-thiol	N-tert-butylbenzo-thiazole-2-sulphenamide	N-cyclohexylbenzo-thiazole-2-sulphenamide	N,N-dicyclohexyl benzothiazole-2-sulphenamide	Di(benzothiazol-2-yl) disulphide	N-1,3-dimethylbutyl-N'-phenyl-p-phenylene-diamine	N,N'-bis-(dimethyl-pentyl) 1,4-benzenedia mine	Dicyclohexyl amine
MR 8370	Råö	Air	pg/m3	<0.6	*	<0.9	<1	<2	<5	*	15
MR 8364	Råö	Air	pg/m3	<0.6	*	<0.9	<1	<2	<5	*	15
MR 8361	Stockholm, Valhallavägen 81	Air	pg/m3	<0.2	*	<0.4	<0.4	<0.7	<2	*	29
MR 8362	Stockholm, Valhallavägen 81	Air	pg/m3	<0.3	*	<0.5	<0.5	<0.9	<2	*	6.6
MR 8404	Borås	Air	pg/m3	<0.07	*	<0.1	<0.1	<0.2	<0.5	*	8.6
MR 8405	Borås	Air	pg/m3	<0.1	*	<0.2	<0.2	<0.3	<0.8	*	4.1
MR 8455	Stenungsund	Air	pg/m3	<0.2	*	<0.3	<0.4	<0.7	<2	*	30
MR 8456	Stenungsund	Air	pg/m3	<0.3	*	<0.5	<0.6	<1	<3	*	82
MR 8363	Råö	Deposition	ng/m2 Day	<0.3	*	<0.4	<0.4	<0.8	<2	*	160
MR 8374	Råö	Deposition	ng/m2 Day	<0.3	*	<0.5	<0.6	<1	<3	*	18
MR 8415	Stockholm, Valhallavägen 81	Deposition	ng/m2 Day	<0.07	*	<0.1	53	<0.2	480	*	110
MR 8416	Stockholm, Valhallavägen 81	Deposition	ng/m2 Day	<0.06	*	<0.09	<0.1	<0.2	<0.4	*	770
MR 8217	Gårdsjön	Surface water	ng/L	6.1	*	<2	<3	<5	<2	*	<2
MR 7953	Sandsjön	Surface water	ng/L	<6	*	<7	<1	<3	29	*	<11
MR 8423	Tärnan	Surface water	ng/L	<10	*	<0.4	<3	<2	<0.5	*	<3
MR 8158	Viskan, Downstream Gässlösa	Surface water	ng/L	19	*	<7	<1	<3	180	*	41
MR 8159	Viskan, Upstream Gässlösa	Surface water	ng/L	15	*	<7	<1	<3	190	*	49
MR 7959	Årstaviken	Surface water	ng/L	<10	*	<0.4	<3	<2	<0.5	*	18
MR 7967	Riddarfjärden	Surface water	ng/L	<10	*	<0.4	<3	<2	<0.5	*	6.4
MR 8027	Stockholm, Görveln	Surface water	ng/L	<3	*	<2	<3	<5	<2	*	<2
MR 8028	Stockholm, Norsborg	Surface water	ng/L	<3	*	<2	<3	<5	<2	*	<2
MR 8218	Stenungsund, Stenungs torg	Surface water	ng/L	5.7	*	<2	<3	<5	<2	*	11
MR 8219	Stenungsund, Fiskeviken St Askö	Surface water	ng/L	<3	*	<2	<3	<5	<2	*	<2
MR 7674	Gårdsjön	Sediment	ng/g DW	<0.8	*	<0.5	<1	<0.6	<0.5	*	<0.2
MR 7954	Sandsjön	Sediment	ng/g DW	<0.8	*	<0.5	<1	31	<0.6	*	<0.2

Sample ID	Station	Matrix	Unit	MBT	TBS	CBS	DBS	DBD	DPP	BBD	DCHA
MR 8265	Tärnan	Sediment	ng/g DW	<0.8	*	<0.5	<1	3.8	<0.6	*	<0.2
MR 7960	Årstaviken	Sediment	ng/g DW	<0.8	*	<0.5	<1	<0.6	<0.5	*	0.77
MR 7962	Stora Essingen	Sediment	ng/g DW	<0.8	*	<0.5	<1	<0.6	<0.6	*	0.37
MR 7968	Långholmen/Riddarfjärden	Sediment	ng/g DW	<0.8	*	<0.5	<1	<0.6	<0.6	*	<0.2
MR 8875	Ekerö, 6 m fr road	Crops (wheat)	ng/g WW	<0.2	*	<1	<0.1	-	-	*	<0.1
MR 8876	Ekerö, 170 m fr road	Crops (wheat)	ng/g WW	<0.1	*	<0.9	<0.1	-	-	*	<0.1
MR 8877	Ekerö, 300 m fr road	Crops (wheat)	ng/g WW	<0.2	*	<1	<0.1	-	-	*	<0.1
MR 8878	Ekerö, 1500 m fr road	Crops (wheat)	ng/g WW	<0.1	*	<0.9	<0.1	-	-	*	<0.1
MR 8220	Gårdsjön	Soil	ng/g DW	<0.7	*	<0.4	<1	30	<0.5	*	<0.2
MR 8434	Stockholm, Valhallavägen	Soil	ng/g DW	<0.7	*	<0.4	<0.9	<0.5	<0.5	*	0.17
MR 8435	Stockholm, Humlegården	Soil	ng/g DW	<0.7	*	<0.4	<1	<0.5	<0.5	*	2.0
MR 8114	Salem, amine gradient 10 m	Soil	ng/g DW	<0.6	*	<0.4	<0.9	<0.4	<0.4	*	3.3
MR 8115	Salem, amine gradient 100 m	Soil	ng/g DW	<0.8	*	<0.4	<1	<0.5	<0.5	*	<0.2
MR 8116	Salem, amine gradient 500 m	Soil	ng/g DW	<0.6	*	<0.3	<0.8	<0.4	<0.4	*	0.52
MR 8428	Valön Fjällbacka	Blue mussel	ng/g DW	<5	*	650	<2	-	-	*	2.5
MR 8429	Nidingen	Blue mussel	ng/g DW	<7	*	530	<3	-	-	*	<4
MR9052	Grebbestad (Preemraff)	Blue mussel	ng/g DW	23	*	470	<4	-	-	*	5.4
MR 8601	Stenungsund, Marina	Blue mussel	ng/g DW	4.0	*	230	<7	-	-	*	3.0
MR 8602	Stenungsund, N harbour outlet	Blue mussel	ng/g DW	18	*	160	<1	-	-	*	<2
MR 8603	Stenungsund, SW Jordhamnsviken	Blue mussel	ng/g DW	15	*	220	<1	-	-	*	<1
MR 8604	Stenungsund, E Jordhamnsviken	Blue mussel	ng/g DW	16	*	130	<1	-	-	*	<1
MR 8605	Stenungsund, Harbour	Blue mussel	ng/g DW	7.7	*	190	<0.7	-	-	*	3.7
MR9049	Hamrevik, (Preemraff)	Blue mussel	ng/g DW	59	*	1040	<13	-	-	*	18
MR9050	Edsvik, (Preemraff)	Blue mussel	ng/g DW	11	*	400	<2.5	-	-	*	<1
MR9051	Produktkaj, (Preemraff)	Blue mussel	ng/g DW	17	*	340	<2.3	-	-	*	<1
MR 8414	Sandsjön	Fish	ng/g DW	6.3	*	7.4	<0.7	-	-	*	<0.5
MR 8266	Tärnan	Fish	ng/g DW	4.5	*	9.7	<0.4	-	-	*	<0.3
MR 8388	Gårdsjön	Fish	ng/g DW	<0.7	*	27	<0.5	-	-	*	<0.3
MR 7969	Årstaviken	Fish	ng/g DW	<1	*	12	<0.6	-	-	*	<0.4
MR 7972	Långholmen/Riddarfjärden	Fish	ng/g DW	<1	*	12	<0.6	-	-	*	<0.4
MR 8400	Henriksdal WWTP	Fish	ng/g DW	5.9	*	5.0	<0.6	-	-	*	<0.4
MR 8402	Stockholm, Biskopsudden	Fish	ng/g DW	7.4	*	5.8	<0.6	-	-	*	<0.4
MR 8403	Stockholm, Torsbyfjärden	Fish	ng/g DW	5.6	*	6.3	<0.6	-	-	*	<0.4
MR 8038	Årsta	Storm water	ng/L	<6.2	*	<7	<1	<3	<3	*	40
MR 8156	Borås, Busstorget	Storm water	ng/L	204	*	<7	<1	<3	<3	*	990

Sample ID	Station	Matrix	Unit	MBT	TBS	CBS	DBS	DBD	DPP	BBD	DCHA
MR 8157	Borås, Knallelandet	Storm water	ng/L	41	*	<7	<1	<3	210	*	105
MR 8039	Huddinge	Storm water	ng/L	<6.2	*	<7	<1	<3	<3	*	<11
MR 8058	Landfill 1	Effluent landfill	ng/L	103	*	<0.4	19	<2	<0.5	*	36
MR 8059	Landfill 3	Effluent landfill	ng/L	84	*	<0.4	18	<2	<0.5	*	71
MR 8004	Gässlösa WWTP	Effluent	ng/L	<6	*	<7	<1	<3	<3	*	55
MR 8006	Öhn WWTP	Effluent	ng/L	59	*	<0.4	<3	<2	<0.5	*	42
MR 8164	Käppala WWTP	Effluent	ng/L	57	*	<0.4	<3	<2	<0.5	*	190
MR 8211	Ryaverken WWTP	Effluent	ng/L	35	*	<7	<1	<3	<3	*	230
MR 8232	Henriksdal WWTP	Effluent	ng/L	15	*	<0.4	<3	<2	<0.5	*	94
MR 8005	Gässlösa WWTP	Sludge	ng/g DW	22	*	<0.4	<1	<0.5	<0.5	*	3.1
MR 8007	Öhn WWTP	Sludge	ng/g DW	21	*	<0.4	<1	<0.5	<0.5	*	5.0
MR 8165	Käppala WWTP	Sludge	ng/g DW	20	*	<0.4	<1	<0.5	<0.5	*	2.1
MR 8212	Ryaverken WWTP	Sludge	ng/g DW	10	*	<0.4	<1	<0.6	<0.5	*	15
MR 8234	Henriksdal WWTP	Sludge	ng/g DW	25	*	<0.4	<1	<0.6	27	*	9.7

Individual results, Benzotriazoles

Sample ID	Umeå ID	Station	Matrix	Unit	UV328	UV329	UV320	UV327	UV234	UV P	UV360
					2-(2H-benzotriazol-2-yl)-4,6-ditert-pentylphenol	2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol	2-(benzotriazol-2-yl)-4,6-di-tert-butylphenol	2,4-di-tert-butyl-6-(5-chloro-benzotriazol-2-yl)phenol	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	2-(benzotriazol-2-yl)-4-methylphenol	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol
MR 8370	3411:27	Råö	Air	ng/m3	<0.3	1.0	<0.2	0.40	<0.3	2.4	0.40
MR 8364	3411:26	Råö	Air	ng/m3	<0.4	1.5	0.44	9.2	<0.4	11	<0.48
MR 8361	3411:25	Stockholm, Valhallavägen 81	Air	ng/m3	<0.06	3.0	<0.03	0.75	<0.05	2.1	<0.07
MR 8362	3411:24	Stockholm, Valhallavägen 81	Air	ng/m3	<0.2	<0.15	0.67	25	<0.2	5.2	<0.3
MR 8404	3411:23	Borås	Air	ng/m3	<0.2	<0.2	<0.1	2.4	<0.2	1.4	<0.3
MR 8405	3411:22	Borås	Air	ng/m3	<0.01	0.056	0.024	0.57	<0.01	0.90	<0.01
MR 8455	3311:56	Stenungsund	Air	ng/m3	<0.01	0.015	<0.01	<0.01	<0.01	0.081	<0.01
MR 8456	3311:57	Stenungsund	Air	ng/m3	<0.02	<0.02	<0.02	<0.02	<0.02	0.065	<0.02
MR 8363	3411:19	Råö	Deposition	ng/m2 day	<200	<100	<100	318	<20	<30	<30
MR 8374	3411:21	Råö	Deposition	ng/m2 day	<100	82	<70	<100	<100	<100	<100
MR 8415	3411:28	Stockholm, Valhallavägen 81	Deposition	ng/m2 day	<80	157	<40	303	<70	860	<100
MR 8416	3411:29	Stockholm, Valhallavägen 81	Deposition	ng/m2 day	<70	331	<40	234	<70	262	<100
MR 8217	3411:47	Gårdsjön	Surface water	ng/L	1.3	1.1	<0.03	0.13	<0.07	<0.08	<0.09
MR 7953	3411:46	Sandsjön	Surface water	ng/L	10	0.25	0.55	0.11	<0.06	<0.09	0.16
MR 8158	3411:49	Viskan, Downstream Gässlösa	Surface water	ng/L	4.1	0.28	<0.03	<0.08	<0.07	18	<0.1
MR 8159	3411:48	Viskan, Upstream Gässlösa	Surface water	ng/L	1.7	0.8	<0.03	<0.08	<0.07	22	<0.09
MR 7959	3411:44	Årstaviken	Surface water	ng/L	3.4	0.54	0.68	0.39	<0.08	<0.1	<0.1
MR 7967	3411:45	Riddarfjärden	Surface water	ng/L	3.2	2.4	0.94	0.26	<0.07	15	<0.1
MR 7674	3411:51	Gårdsjön	Sediment	µg/g DW	1.3	<0.5	0.56	1.6	<0.6	1.6	<0.8
MR 7954	3411:16	Sandsjön	Sediment	µg/g DW	<10	33	<0.6	18	<9	<11	<12
MR 8265	3411:11	Tärnan	Sediment	µg/g DW	0.65	0.81	0.16	2.1	<0.2	<0.3	0.46
MR 7960	3411:17	Årstaviken	Sediment	µg/g DW	<0.7	<0.4	3	35	<0.6	5.1	2.9
MR 7962	3411:18	Stora Essingen	Sediment	µg/g DW	0.83	5.4	0.9	8.4	<0.2	<0.3	<0.3
MR 7968	3411:12	Långholmen/Riddarfjärden	Sediment	µg/g DW	1.2	1.9	0.18	1.6	<0.3	<0.3	0.42

Sample ID	Umeå ID	Station	Matrix	Unit	UV328	UV329	UV320	UV327	UV234	UV P	UV360
MR 8220	3411:55	Gårdsjön	Soil	µg/g DW	<0.7	1.7	0.91	<0.6	<0.7	2.3	<0.9
MR 8434	3411:54	Stockholm, Valhallavägen	Soil	µg/g DW	<0.4	0.79	<0.2	3.7	<0.3	0.38	<0.4
MR 8435	3411:53	Stockholm, Humlegården	Soil	µg/g DW	0.74	<0.2	<0.1	0.77	<0.2	<0.2	<0.3
MR 8116	3411:5	Salem, amine gradient 500 m	Soil	µg/g DW	<0.7	3.7	<0.4	0.66	<0.6	<0.7	<0.8
MR 8387	3411:4	Gårdsjön	Fish	µg/g DW	<1.5	<1	<0.9	9.8	<1.4	<1.7	<1.9
MR 8414	3411:3	Sandsjön	Fish	µg/g DW	<0.3	1	<0.1	2.3	0.26	<0.3	<0.3
MR 7969	3411:1	Årstaviken	Fish	µg/g DW	<1.4	2.5	<0.8	<1.2	<1.3	<1.6	<1.8
MR 7972	3411:2	Långholmen/Riddarfjärden	Fish	µg/g DW	<0.6	2	<0.3	4	<0.5	4.2	<0.7
MR 8038	3411:32	Årsta	Storm water	ng/L	0.38	<0.07	0.73	0.14	0.2	10	0.17
MR 8156	3411:33	Borås, Busstorget	Storm water	ng/L	<.1	<0.06	<0.03	0.13	<0.08	5.9	<0.1
MR 8157	3411:34	Borås, Knallelandet	Storm water	ng/L	1.3	<0.04	<0.03	<0.07	0.06	9	<0.08
MR 8039	3411:31	Huddinge	Storm water	ng/L	0.19	<0.06	<0.04	0.17	0.31	1.1	0.28
MR 8058	3411:50	Landfill 1	Effluent landfill, particles	µg/g DW	3.1	6.1	<0.7	4.3	<1.2	1.4	<1.6
MR 8058	3411:36	Landfill 1	Effluent landfill	ng/L	7	<0.08	<0.5	1.3	0.16	<0.1	<0.1
MR 8054	3411:37	Landfill 2	Effluent landfill	ng/L	23	<0.08	7.3	0.45	<0.1	<0.1	<0.1
MR 8059	3411:35	Landfill 3	Effluent landfill	ng/L	91	17	23	<0.2	0.5	<0.2	<0.3
MR 8437	3411:52	Henriksdal WWTP	Effluent, particles	µg/g DW	<110	<72	<61	270	<99	<90	<130
MR 8004	3411:38	Gässlösa WWTP	Effluent	ng/L	11	2.8	4	0.21	<0.09	<0.1	<0.1
MR 8006	3411:39	Öhn WWTP	Effluent	ng/L	14	1.2	<0.04	0.48	0.11	33	<0.1
MR 8008	3411:40	Bollebygd WWTP	Effluent	ng/L	9.1	2.2	<0.04	0.28	<0.09	<0.1	<0.1
MR 8164	3411:42	Käppala WWTP	Effluent	ng/L	15	0.87	<0.05	0.12	<0.1	15	<0.1
MR 8269	3411:43	Ellinge WWTP	Effluent	ng/L	6.8	4.9	<0.04	<0.1	<0.09	<0.1	<0.1
MR 8005	3411:14	Gässlösa WWTP	Sludge	µg/g DW	<0.6	8.9	1.6	5.7	7.3	17	16
MR 8007	3411:9	Öhn WWTP	Sludge	µg/g DW	2.4	2.3	0.84	0.54	6.6	9.6	13
MR 8009	3411:8	Bollebygd WWTP	Sludge	µg/g DW	3.8	9.5	1.8	10	4.9	8.5	23
MR 8119	3411:7	Nolhaga WWTP	Sludge	µg/g DW	37	<0.2	0.88	2.5	3.3	6.9	5
MR 8165	3411:15	Käppala WWTP	Sludge	µg/g DW	<0.4	28	0.95	<0.4	3.8	18	10
MR 8212	3411:13	Ryaverken WWTP	Sludge	µg/g DW	27	15	<0.3	17	5.6	11	6.2
MR 8234	3411:10	Henriksdal WWTP	Sludge	µg/g DW	<1	12	<0.5	1.2	6.1	13	15
MR 8270	3411:6	Ellinge WWTP	Sludge	µg/g DW	<0.1	13	2	2.3	2.1	9.7	4.6