RAPPORT

Results from the Swedish National Screening Programme 2007

Sub report 1: Amines

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Report Summary

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Sub report 1: Amines

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Results from the Swedish National Screening Programme 2007

Sub report 1: Amines

Summary

Amines are important chemicals that are being used in a vast number of chemical processes. As an assignment from the Swedish Environmental Protection Agency, a screening study of a selected number of amines has been performed. The overall objective of the screening was to determine the concentrations of amines in a variety of media in the Swedish environment.

Keywords

Amines, Dicyclohexylamine, DCHA, IDDP, diphenylamine, NCBA, Screening, air, water, sediment, sludge, leachate, storm-water, traffic

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Summary

Amines are an important group of organic compounds that are being used in a vast number of chemical processes and applications. The amines included in this study (5 altogether) encompass aromatic as well as cyclic and aliphatic amines. These amines are primarily used in the paint and glue industry, as binding agents in asphalt, as conservation (antioxidizing) agents in rubber, as synthesis chemicals in the production of fungicides, lubricants and fuel additives, as well as agents in paper production, surface chemicals and bleach chemicals, to mention a few applications.

As an assignment from the Swedish Environmental Protection Agency, a screening study of organic amines has been performed. The overall objective of the screening was to determine concentrations in a variety of media in the Swedish environment. A national sampling program (58 samples) was combined with an extensive regional program administered by several county administrative boards (37 samples). Sample types were air, waste water, sludge, storm water, ground water, surface water, soil and sediment.

Amines were detected in most samples and matrices and dicyclohexylamine (DCHA) in particular, was detected in 78 % of all samples (74 out of 94 samples). The other amines were found occasionally and mostly in lower concentrations.

Interestingly several amines were detected in air samples from background locations, indicating that air is an important transport medium for the dispersion of organic amines in the environment.

Since several of the amines included are used in relation to traffic, the sampling program included sampling sites such as road sides and storm water from urban impervious surfaces. The results indicated that diffuse dispersion of DCHA from traffic and urban activities seems to be most important for the occurrence of DCHA in the Swedish environment.

The aliphatic amine pentaethylenehexamine (PEHA) proved to be very difficult to analyse and thus, the results concerning that particular compound can only be considered as indicative. Further method development is needed before any conclusions can be drawn regarding the dispersion of PEHA in the Swedish environment.

The concentrations of DCHA found in surface waters from urban areas and industrial recipients were lower than reported PNEC-values derived from the set of toxicity data. Thus, DCHA at present levels is not expected to cause adverse effects in the water phase of the recipients. However, the high detection frequency of DCHA in this study suggests that this particular amine is spread into all compartments of the Swedish environment and should therefore be monitored further.

Sammanfattning

På uppdrag av Naturvårdsverket har en screeningstudie av ett antal industriellt relevanta aminföreningar utförts. Sammanlagt har fem olika aminföreningar ingått i studien; en alifatisk polyamin (pentaetylenhexamin, PEHA, CAS 4067-16-7), en di-cyklisk, mättad amin (dicyklohexylamin, DCHA, CAS 101-83-7), samt tre aromatiska aminer (N-cyklohexyl-2-bensotiazolamin, NCBA, CAS 28291-75-0, 4-isopropyldifenylamin, IPPD, CAS 101-72-4 och difenylamin, DPA, CAS 122-39-4).

Trots att de fem aminerna särskiljer sig i all väsentlighet ifrån varandra avseende de fysikalisk-kemiska egenskaperna har samtliga föreningar kunnat knytas till biltrafik, vägar och trafikrelaterade material. Exempelvis används PEHA som bindemedel i vägasfalt, NCBA bildas oavsiktligt i när bildäcksgummi vulkaniseras, IPPD används bl a som antioxidant i bildäcksgummi, DPA har ett flertal användningsområden av vilka ett är som smörjmedel i olika smörjoljor i fordon. Slutligen kan det konstateras att även DCHA kan knytas till trafikrelaterade emissioner då även denna förening används vid vulkaniseringsprocessen. DCHA och DPA har givetvis ett stort antal andra användningsområden och bör betraktas som industriella baskemikalier. Det är således DCHA och DPA som tidigare detekterats och uppmätts i tidigare genomförda miljöundersökningar internationellt.

Baserat på ämnenas egenskaper (t ex log Kow-värden, vattenlöslighet och ångtryck) i kombination med de listade användningsområdena sammanställdes en provtagningsplan innefattandes ett stort antal olika matriser och provlokaler (tabell 1). Stenungsund identifierades som en potentiell punktkälla då en betydande del av svensk petroleum- och plastindustri är lokaliserad dit. Vidare misstänktes trafikrelaterade emissioner kunna stå för ett betydande spridningbidrag av dessa ämnen, då främst genom avnötning ifrån material och trafikytor, varför en större motorväg och den omgivande miljön inkluderades.

Tabell 1. Nationellt provtagningsprogram för aminer.

Typ av lokal	**Luft**	**Sediment**	**Ytvatten**	**Grundvatten**	**Dagvatten**	**ARV in**	**ARV ut**	**Slam**	**Jord**	**Totalt**
Bakgrundsområden	3	2	2	4					1	**12**
Påverkade områden										
Punktkällor										
A: Stenungsund		3	3						2	**8**
B: Vägar									4	**4**
C: Deponier							3			**3**
Diffus spridning										
Urbana områden	6	3	3		8				3	**23**
ARV-anläggningar						3	2	3		**8**
Totalt	**9**	**8**	**8**	**4**	**8**	**3**	**5**	**3**	**10**	**58**

Fordon och gummi/plastmaterial ursprungligen tillverkade för fordonsindustrin riskerar alltid att hamna på deponier i slutet av livscykeln varför även deponier identifierades som potentiellt intressant.

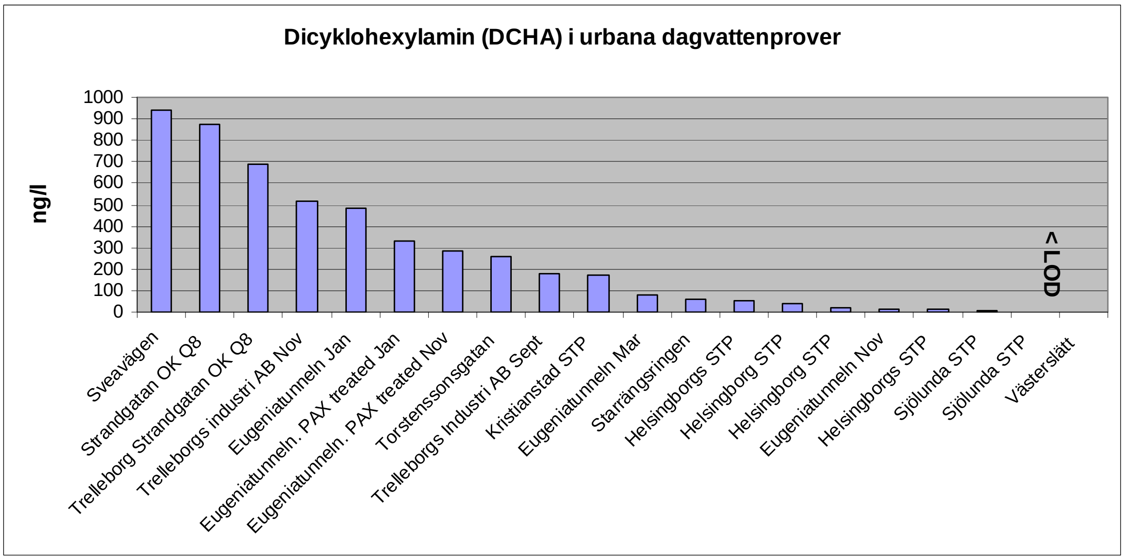
Till dessa 58 prover skall även läggas 37 regionala prover, insamlade av länsstyrelserna och skickade till IVL för upparbetning och slutbestämning. De regionala proverna innefattade 5 ingående vattenprover, 10 utgående vattenprover, 10 slamprover och 12 dagvattenprover.

Då tre av de ingående aminerna i denna studie ej tidigare varit föremål för publicerade studier kring förekomst (PEHA, NCBA och IPPD) krävdes en större insats m a p metodutveckling. Under denna period kunde det tyvärr konstateras att tillgänglig teknik för att haltbestämma miljöprover

m a p PEHA ej finns för närvarande. Detta är en synnerligen komplicerad och reaktiv molekyl som vid de allra flesta pH-värden är katjonisk eller t om polykatjonisk. Det innebär att molekylen tenderar att adsorberas elektrostatiskt på alla fasta ytor såsom glasutensilier på laboratoriet eller på partiklar i slam, sediment och jord. Extraktionsutbytet för PEHA torde således bli oacceptabelt lågt när denna typ av provmatriser skall upparbetas. Den använda analysmetodiken betraktas således som semi-kvantitiativ m a p PEHA, och endast vattenprover har ingått i studien av denna amin.

Resultat

Den amin som genomgående detekterades mest frekvent och i de högsta koncentrationerna var dicyklohexylamin (DCHA). DCHA förekom i alla provmatriser och ifrån alla provlokaler. 78 % (74 prover av 95) av alla insamlade prover innehöll detekterbara halter av DCHA. I exempelvis urbana dagvatten, som ju insamlar stora mängder partiklar ifrån materialförslitning på, i och omkring hårdgjorda ytor, detekterades DCHA i alla prover utom ett. Hypotesen att vägtrafikfordon påverkar emissionsmönstret för någon/några av de i studien ingående aminerna understöds av dessa resultat (se bild nedan).



Figur 1. DCHA i dagvatten. LOD < 6 ng/l.

Av de övriga aminerna detekterades IDDP mycket sällan och förekom endast i slamprover ifrån avloppsreningsverk (3 prover av 13).

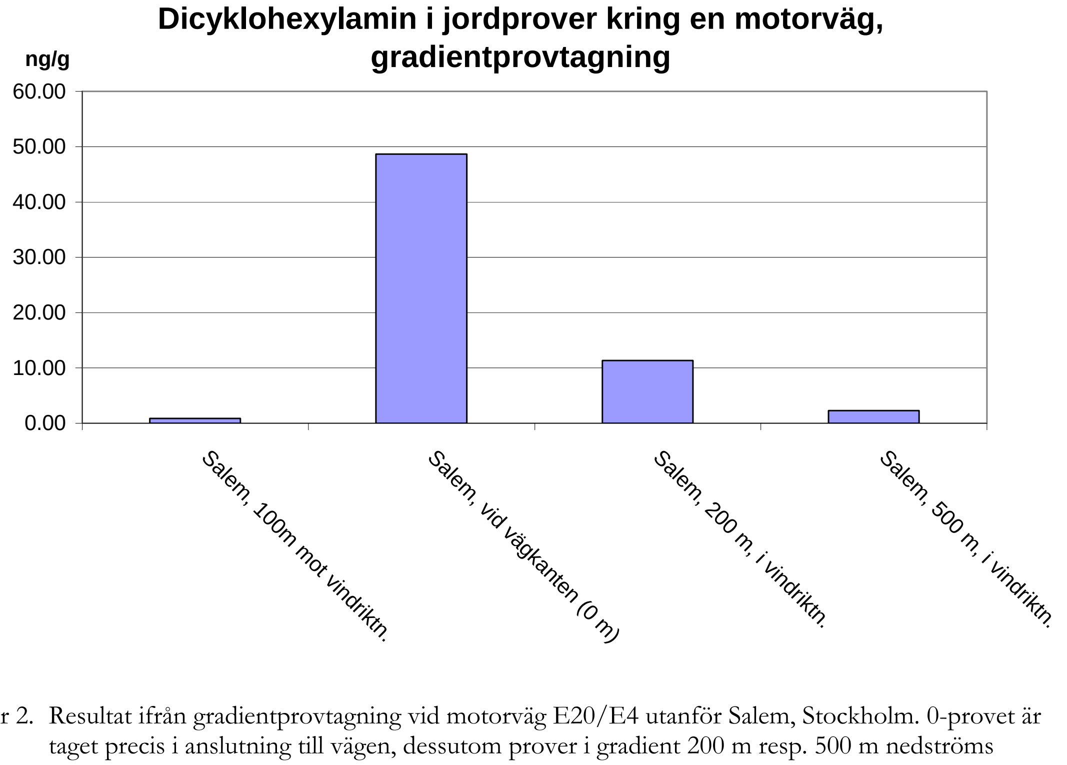
Vidare detekterades NCBA i bl a luft, ytvatten, dagvatten, slam och sediment. Detektionsfrekvensen för NCBA var ca 10 % och halterna är jämförbara med DCHA, d v s låga.

DPA, som delvis liknar DCHA m a p fysikaliska egenskaper (t ex log Kow mm) detekterades endast i en handfull prover t ex i ytvatten från urbana områden, dagvatten och sediment.

PEHA detekterades i ett antal vattenprover (däribland grundvatten vilket förefaller vara mindre troligt) men analysmetodiken är f n för omogen för att man säkert skall kunna dra några slutsatser kring detta ämnes eventuella förekomst i miljön.

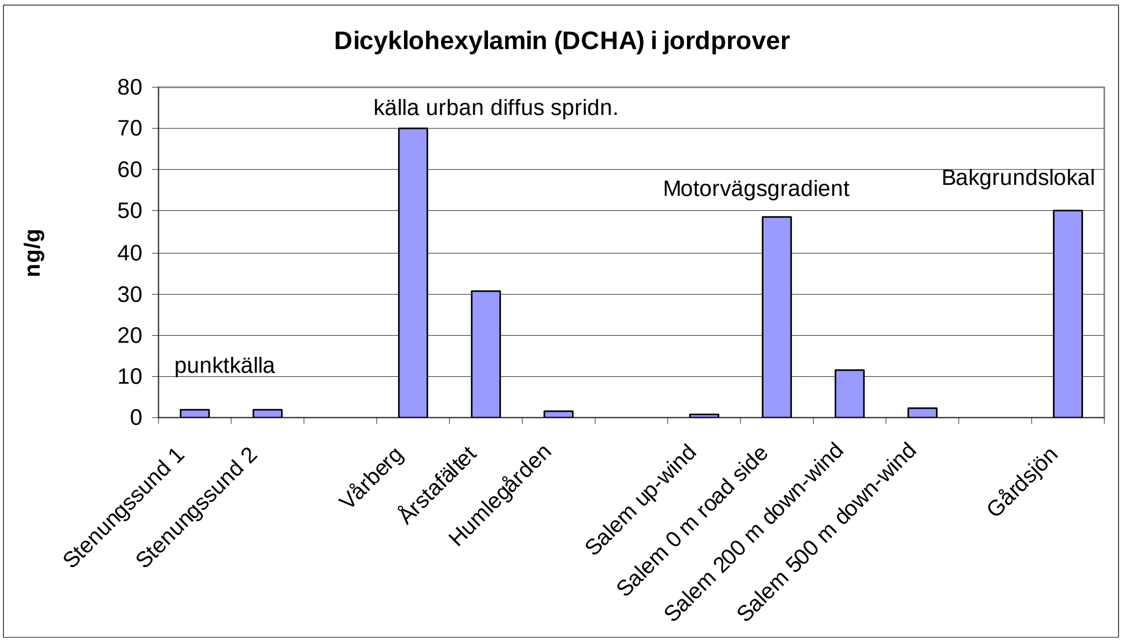
Avseende DCHA visar studien på stora variationer i de detekterade halterna, t ex varierar halten av DCHA i dagvatten mellan <5-940 ng/l. Även i slamprover påvisades en mycket stor variationsbredd m a p DCHA; 5-770 ng/g TS.

Associationen mellan dessa aminer och fordonstrafik-vägar undersöktes i samband med provtagningen av jord i närheten av ett större motorvägskluster där jorden provtogs i ett gradientförfarande med stigande avstånd ifrån vägkanten relativt den förhärskande vindriktningen. Halterna av DCHA i jordproverna klingade också av och torde därmed avspegla emissionsbidraget ifrån fordonstrafiken (se bild nedan)



Figur 2. Resultat ifrån gradientprovtagning vid motorväg E20/E4 utanför Salem, Stockholm. 0-provet är taget precis i anslutning till vägen, dessutom prover i gradient 200 m resp. 500 m nedströms ”0-punkten” (i den förhärskande vindriktningen), samt ett referensprov ett 100 meter uppströms 0-punkten (mot den förhärskande vindriktningen).

För DCHA torde den urbana diffusa spridningen vara dem mest betydande för förekomst av detta ämne i miljön. Exempelvis är halterna av DCHA genomgående högre i jordprover ifrån Stor-Stockholm än de halter som uppmätts i jord ifrån Stenungsund (se bild nedan).



Slutsatser

Den viktigaste slutsatsen ifrån undersökningen är att dicyklohexylamin är frekvent förekommande i den svenska miljön).

De halter som uppmätts i utgående, renat avloppsvatten och i ytvatten är inte associerade med någon uttalad miljörisk för akvatiska arter (MEC/PNEC<<1). Dock är detta riskbedömningsförfarande ytterst rudimentärt och det kan mycket väl finnas ett flertal enskilda reningsverk vars recipienter de facto påverkas av DCHA i det utgående vattnet, speciellt recipienter där volymsflödet ifrån reningsverket utgör en betydande fraktion (mer än 10 %) av recipientens totala vattenföring.

En annan mycket viktig slutsats ifrån screeningundersökningen av aminer är att dessa ämnen tycks spridas över stora områden, via luft som transportmedium. Att främst DCHA, men även NCBA, detekteras i luftprover ifrån bakgrundsområden visar med önskvärd tydlighet att användningsområdet i kombination med egenskaper i dessa fall ger upphov till en stor spridning.

De halter av aminerna som uppmätts i utgående vatten ifrån reningsverk, dagvatten och även slam uppvisar en mycket stor variationsbredd (i princip tre tiopotenser) varför riskbedömningen ytterligare försvåras.

Det är motiverat att föreslå utökade mätningar av DCHA i ett flertal matriser för att få en mer fördjupad kunskap om var i miljön DCHA ansamlas. Det är också önskvärt att i en sådan studie även inkludera biotaprovtagning, t ex av fisk. Upptag i fisk skulle kunna vara en tänkbar exponeringsväg även för människa.

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1 Introduction

As an assignment from the Swedish Environmental Protection Agency a "Screening Study" of amines, esters, pigments, and linear alkyl benzene sulfonate (LAS), as well as silver, has been performed. These substances are emitted and distributed in the environment via a variety of sources, e.g. different point sources and/or diffusive sources. Some of them are also used in consumer products.

The overall objectives of the screening studies are to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. The results are given in five sub-reports according to Table 1.

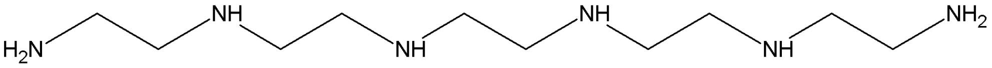
Table 1. Substances / substance groups included in the screening

Substance / Substance group	Sub-report #
Amines: 3,6,9,12-Tetraazatetradecane-1,14-diamine N-cyclohexyl-2-benzothiazolamine (NCBA) N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) N-Phenyl-benzeneamine Dicyclohexylamine	1
Esters: Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	2
Pigments: Pigment yellow 1 (CI 11680) Pigment orange 5 (CI 12075) Pigment red 53:1 (CI 15585:1) Pigment red 170 (CI 12475)	3
Linear alkyl benzene sulfonate (LAS)	4
Silver	5

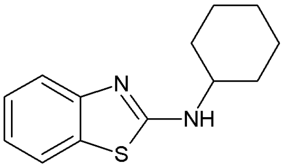
This sub-report considers the screening of the amines. Amines are organic compounds containing nitrogen. The amines included in this screening study are specified in Table 2 where also synonyms and abbreviations are given together with CAS-numbers. Their corresponding chemical structures are shown in Figure 1.

Table 2. Amines in this study.

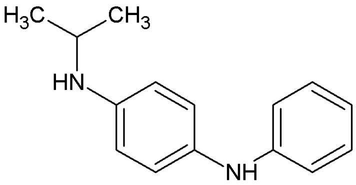
Name	**Abbreviation / synonyms**	**CAS#**
3,6,9,12-Tetraazatetradecane-1,14-diamine	Pentaetylenehexamine PEHA	4067-16-7
N-Cyclohexyl-2-benzothiazolamine	NCBA	28291-75-0
N-Isopropyl-N'-phenyl-p-phenylenediamine	4-(Isopropylamino)-diphenylamine, IPPD	101-72-4
N-Phenyl-benzeneamine	Diphenylamine, DPA	122-39-4
Dicyclohexylamine	DCHA	101-83-7



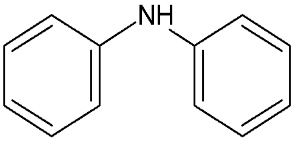
Pentaetylenehexamine, PEHA, 4067-16-7



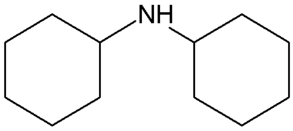
N-Cyclohexyl-2-benzothiazolamine,
NCBA, 28291-75-0



N-Isopropyl-N'-phenyl-p-phenylenediamine, IPPD, 101-72-4



Diphenylamine, DPA, 122-39-4



Dicyclohexylamine, DCHA, 101-83-7

Figure 1. Structures of the amines

2 Chemical Properties, fate and toxicity

2.1 Properties and fate

The physical and chemical properties of the amines included in the study are given in Table 3.

Table 3. The physical- and chemical properties of the amines. Unless otherwise noted, the values are from experimental data from ChemID Plus Advanced.

Name	**CAS#**	**log K_{ow}**	**Henry's law constant ((atm*m^3) / mol)**	**Molecular weight (g/mol)**	**Melting point (°C)**	**Boiling point (°C)**	**Vapor pressure (mm Hg)**	**Water solubility (mg/l)**
Pentaethylene-hexamine	4067-16-7	-2.9^{a}	$8.36E-24^{e}$	232.373	-35^{d}	~350	$<0.075^{d}$ (20°C)	$1kg/l^{e}$
NCBA	28291-75-0	4.2^{f}	-	231.4	-	-	-	-
IPPD	101-72-4	3.6^{a}	$1.4E-9^{a}$	226.321	74	166^{b}	$7.11E-5^{a}$	$\sim 15^{c}$
Diphenyl amine	122-39-4	3.5	$2.7E-6^{a}$	169.226	52.9	302	$6.39E-4^{h}$ (25°C)	53
Dicyclohexyl amine	101-83-7	3.0^{a}	$5.5E-5^{a}$	181.32	20	256	0.0338 (25°C)	800^{g}

a – ChemIDPlus Advanced calculated value

b – ChemicalLand 2008

c – OECD 2000

d – Akzo Nobel, 2004

e – SRS Phys Prop Database

f – Kumata et al. 2002

g – ECB 2000

h - FAO 2001

The screening includes five amines; two aliphatic and three aromatic, see Figure 1.

Pentaethylenehexamine, PEHA, is an aliphatic amine which is very hydrophilic with its negative log K_{OW} which can be compared to the log $K_{OW} \geq 3.0$ for the other four amines. The polar nature of pentaethylenehexamine makes it likely that it will mainly partition into the water phase. It is not readily biodegradable (Akzo Nobel 2004).

The aromatic amines are; NCBA, IPPD and diphenylamine while PEHA and dicyclohexylamine, are aliphatic/cyclic. Dicyclohexylamine and the aromatic amines are lipophilic with log K_{OW} -values between 3.0 and 4.2, indicating that they may have bioaccumulation potential.

IPPD undergoes rapid hydrolysis (half-life 2-16 hours) and only a few percent of the original substance remains after 24 hours. No significant mineralisation of IPPD has been shown in sludge or water (OECD 2000). N-Phenylbenzoquinoneimine, 4-hydroxydiphenylamine and isopropylamine have been indentified as hydrolysis products of IPPD (ECB 2004). The quite high log K_{OW}-value of IPPD may indicate a partitioning towards sediment and soil rather than the water phase. The IPPD released to air is quickly degraded according to the OECD SIDS Report but air might still be an important matrix when elucidating the dispersion pathway of this chemical in the environment. Some information on the degradation of IPPD can be gathered from data on a closely related structure analogue of IPPD; 6PPD (4-(dimethyl butylamino)diphenylamine, CAS# 793-24-8) only differing from IPPD in a terminal 2-propyl group. Data in a report by the OSPAR Commission 2005, indicates that 99% of the substance is hydrolysed within 24 hours and the substance undergoes photodegradation as well, absorbing UV-B-radiation of 291 and 350 nm. Degradation experiments of 6PPD show a high rate of primary degradation, but a low mineralisation rate.

Diphenylamine, DPA, is hydrophobic, approximately 1000 times more soluble in hexane than it is in water. It evaporates slowly from surfaces making air a possible pathway of dispersion in the environment (FAO 2001). The half-life of diphenylamine in soil is one to four weeks (Contaminant Information, Diphenyl amine, Ecological Assessment of Storm Impact on Marine Resources). It has a half-life of 350 days in sterile water at 25°C and approximately 60 days in anaerobic conditions using lake water and sediment (FAO 2001). DPA is biodegradable in both aerobic and anaerobic environments. The major product of the anaerobic degradation is aniline, which in turn is degradable in both anaerobic and aerobic conditions. Aerobic degradation of diphenylamine seems to also result in the formation of aniline (Drzyzga et al. 1995; Drzyzga, 2003).

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 being exposed to sunlight. It is very corrosive and reactive with acids, oxidizing agents and chloroformates. A Japanese study comparable with an OECD 301c test (biodegradation in active sludge) resulted in 76.9% degradation of dicyclohexylamine after two weeks. Another study, an OECD 301d test, demonstrated degradation of 0% after 5 days, 72% after 10 days and 96% after 20 days (OECD 2006). Dicyclohexylamine is thus ready biodegradable.

2.2 Toxicity

All amines herein, except NCBA for which there are no publicly available data, are classified as very toxic towards the aquatic environment and organisms (Kemikalieinspektionen 2008). Pentaethylenhexamine causes burns to skin and eyes (Technical Resources International, Inc. 2006), is very corrosive and reactive, but in it self stable.

It has previously been reported that lipophilicity of primary and secondary amines is well correlated to their general toxicity (Brust, K 2001). Pentaethylenehexamine, being very hydrophilic, could according to this study be assumed to have a relatively low toxicity compared to many other secondary amines.

2.2.1 Pentaethylenehexamine, PEHA

Table 4. Toxicity data of pentaethylenehexamine

Species	Test type	Endpoint	Reference
Brachydanio rerio	LC0 96h	100 mg/l	[1]
Bacteria	EC50	>100 mg/l	[1]

[1] – Akzo Nobel 2004

2.2.2 NCBA

No exotoxicological data on NCBA have been found. Since the substance has a log k_{ow} of 4.2, it may very well be bioaccumulative.

2.2.3 IPPD

Table 5. Toxicity data of IPPD

Species	Test type	Endpoint	Reference
Bluegill sunfish	LC50 96h	0.43 mg/l	[1]
Rainbow trout	LC50 96h	0.34 mg/l	[1]
Fathead minnow	LC50 96h	0.41 mg/l	[1]
Fathead minnow	LC50 14d	0.09 mg/l	[1]
Daphnia magna	LC50 48h	1.1 mg/l	[1]
Green algae	EC50 96h	0.4 mg/l	[1]
Green algae	EC50 96h	0.5 mg/l	[1]
Paratanytarsus parthenogenetica	LC50 48h	23 mg/l	[1]

[1] – OECD, 2000

From the data shown on the toxicity of IPPD in Table 5, the lowest endpoint is for Fathead minnow. An LC50 of 0.09 mg/l corresponds to a PNEC of 0.9 µg/l, using a safety factor of 100. The high log K_{ow} of IPPD indicates that it may be bioaccumulative. A reported high hydrolysis rate implies that only a few percent of the original substance is present after a 96 hour test period. Flow-through studies show similar toxicity as static tests, suggesting that IPPD have similar toxicity as its hydrolysis products (OECD 2000).

Several toxicity tests have been performed on the already mentioned structural analogue 6PPD, with the most sensitive being a LC50 (96h) of 0.028 mg on *Oryzias latipe* in a flow through test (6PPD, OSPAR Commission, 2006). This is comparable with the most sensitive test of IPPD.

2.2.4 Diphenylamine, DPA

Table 6. Toxicity data of diphenylamine

Species	**Test type**	**Endpoint**	**Reference**
Oryzias latipes	LC50 24h	4 mg/l	1
Oryzias latipes	LC50 48h	2,2 mg/l	1
Pimephales promelas	LC50 96h	3,79 mg/l	1
Selenastrum capricornutum	EC50 72h	2,17 mg/l	1
Selenastrum capricornutum	NOEC 72h	370 µg/l	1
Daphnia magna	EC50 24h	960 µg/l	1
Daphnia magna	EC50 48h	310 µg/l	1
Daphnia magna	EC50 48h	2 mg/l	1
Leuciscus idus	LC50 48h	>20 mg/l	2
Oryzias latipes	LC50 48h	5.1 mg/l	2
Algae	EC50 72h	0.18 mg/l	2
Daphnia magna	EC50 24h	2.3 mg/l	2
Brachydanio rerio	LC50 48h	2.2 mg/l	3
Leuciscus idus	LC0 48h	20 mg/l	3
Oryzias latipes	LC50 48h	5.1 mg/l	3

[1] – PAN Pesticides Database

[2] – Chemtura, 2006

[3] – The Ecological Assessment of Storm Impacts, Diphenylamin

Diphenylamine has a log K_{ow} of 3.5, but bioaccumulation is not expected in humans since it is transformed into hydroxylated metabolites (Scientific Committee on Health and Environmental Risks, 2008). Tests have however not shown any significant genotoxic or carcinogenic effect. The most sensitive species according to Table 6 is algae with an EC50 (72h) of 0.18 mg/l, from which a PNEC of 0.18 µg/l can be obtained using an assessment factor of 1000.

2.2.5 Dicyclohexylamine, DCHA

Table 7. Toxicity data of dicyclohexylamine

Species	**Test type**	**Reported dose**	**Reference**
Brachydanio rerio	LC50 96h	62 mg/l	1
Brachydanio rerio	LC0 96h	49.2 mg/l	1
Brachydanio rerio	LC100 96h	97.6 mg/l	1
Oryzias latipes	LC50 96h	12 mg/l	1
Oryzias latipes	LC0 96h	8 mg/l	1
Oryzias latipes	LC100 96h	18 mg/l	1
Leuciscus idus	LC0 48h	10 mg/l	1
Leuciscus idus	LC100 48h	20 mg/l	1
Daphnia magna	LC50 48h	8 mg/l	1
Daphnia magna	LC0 48h	3.7 mg/l	1
Daphnia magna	LC100 48h	18 mg/l	1
Daphnia magna	LC50 48h	70.1 mg/l	1
Daphnia magna	LC10 48h	14.8 mg/l	1
Daphnia magna	LC90 48h	>320 mg/l	1
Selenastrum capricornutum	NOEC 72h	2 mg/l	1
Selenastrum capricornutum	LC50 72h	23 mg/l	1
Selenastrum capricornutum	NOEC 72h	0.016 mg/l	1
Selenastrum capricornutum	LOEC 72h	0.031 mg/l	1
Selenastrum capricornutum	EC50 72h	0.38 mg/l	1
Bacteria	EC50 3h	712 mg/l	1
Daphnia magna	NOEC 21 days	0.016 mg/l	1
Daphnia magna	LC50 21 days	1.3 mg/l	1

[1] - OECD 2006

Dicyclohexylamine is toxic to mice and rats by several modes of action but has not shown any significant mutagenic properties. The *Daphnia magna* NOEC of dicyclohexylamine of 0.016 mg/l (Table 7), corresponds to a PNEC of 0.16 µg/l, using a safety factor of 100.

3 Sources and Use

Table 8. Amounts sold/produced/used in Sweden

Substance	**Amount**	**Comment**
Pentaethylenehexamine	196 tonnes of total use in Sweden 2005	1999 to 2004 the used amounts in Sweden were 52 to 285 tonnes
NCBA	1	
IPPD	Confidential since 2002 (Sweden). World-wide production 10 000 – 15 000 tonnes annually	0 to 1 tonnes annually 1999 to 2001
Diphenylamine	7.tonnes sold in Sweden 2005	1999 to 2004 the sold amount in Sweden was 6 to 13 tonnes. EU market volume is about 10 000 tonnes per year[2]
Dicyclohexylamine	6 tonnes total use in Sweden 2005	Increasing trend since 1992

Unless noted otherwise, numbers are from the SPIN database (www.kemi.se)

[1] NCBA is not produced nor used in its traditional sense. The amounts of NCBA non-intentionally produced are not known.

[2] Risk Assessment Report on Diphenylamine, Scientific Committee on Health and Environmental Risks, SCHER 2008

Pentaethylenhexamine has many diverse uses in both consumer products and the industry. It is also a constitutient of asphalt and thus also affiliated with traffic. It is sold as a pure compound or as a mixture containing branched isomers and cyclic compounds with the same number of nitrogen atoms as pentaethylenhexamin.

It is used as a hardener in the paint and glue industry, and as a binding agent in asphalt. Other applications are such as synthesis chemical in the production of fungicides, lubricants and fuel additives, as well as agents in paper production, surface chemicals and bleach chemicals. In 2002, the world-wide production of pentaethylenehexamine was 500 – 5 000 metric tonnes according to the US Environmental Protection Agency (Technical Resources International, Inc. 2005-2006). It is commonly produced via the ethylene dichloride process, in which ethylene dichloride reacts with an excess of ammonia followed by a neutralisation with NaOH. The different products are then separated through distillation.

In car tyre vulcanization accelerator chemicals, **NCBA may** exists as an impurity. It has been considered to be a good marker for vehicle-derived contaminants in the environment (H. Kumata et al. 2000). NCBA is unintentionally produced and minor is known about the amounts of NCBA discharged.

Another constituent in car tyres is **IPPD** that functions as a conservating (antioxidizing) agent in rubber, with an annual production of 10 000 – 15 000 tonnes worldwide (OECD 2000). It is a contact allergen causing dermatitis both when skin is in contact with IPPD directly as well as when skin is in contact with finished products (rubber) containing this chemical. IPPD is made from 4-nitrodiphenylamine and acetone. New tyres for passenger vehicles contain up to 1% IPPD and its analogue 6PPD (4-(dimethylbutylamino)-diphenylamine). The corresponding number for truck tyres is up to 2% (Svensk Däckåtervinning AB). Between 90 and 100 percent of the worn-out tyres in Sweden are collected (Svensk Däckåtervinning AB) starting from 1995. Finland and Germany also collect ≥90% of the worn-out tyres. The fate of these collected tyres in Sweden is (in falling order): energy for cement industry, material replacement, material recycling, heat production, blasting mats, export and re-rubbering. Thus, the full life-cycle of products containing IPPD needs to be considered when studying the pathways of this substance in the environment.

Diphenylamine, DPA, is mostly used as a chemical intermediate in production of other chemicals such as antioxidants, antiozonants and dyes. It is a strong base and very corrosive. It is also a corrosion inhibitor used in lubrication oils in the vehicle industry, as a fungicide as well as a stabilizer in explosives (Drzyzga, 2003). Diphenylamine is toxic to humans causing symptoms similar to those from aniline (headache, drowsiness among others) but is considered less toxic.

Dicyclohexylamine, DCHA, has a very wide use in chemical processes. It is used in the rubber vulcanisation process and as a fuel oil additive, as a chemical intermediate, to mention a few. It can be produced from aniline forming diphenylamine and ammonia. Dicyclohexylamine is also produced from aniline, at high pressure, together with a catalyst. It is a hydrophobic amine used in insectizides, plasticizers, in the metal industry, as a fuel oil additive and as a chemical intermediate. It is affiliated with traffic since it is a component used in the rubber vulcanization process.

4 Previous measurements in the environment

Diphenylamine, and degradation products from dicyclohexylamine, has been detected in soil and ground water near a munition production facility in Germany. Gunpowder plates and discs found at the site had a diphenylamine concentration of 1.4-2.9 g/kg (Drzyzga, 2003).

A study in the Netherlands 1989-1991 analyzed the dicyclohexylamine contents in eight surface waters. The samples contained up to 0.025 µg/l dicyclohexylamine, where six of the samples reported concentrations below the detection limit. An air sampling at five US locations found dicyclohexylamine in one of the two samples from one site (OECD 2006).

5 Sampling

5.1 National program

Table 9. National sampling program

Type	Air	Sediment	Surface water	Ground water	Storm water	Influent water	Effluent water	Sludge	Soil	Total
Background areas	3	2	2	4					1	**12**
Affected areas										
Point Source										
A: Stenungsund		3	3						2	**8**
B: Road									4	**4**
C: Landfills							3			**3**
Diffuse spreading										
Urban areas	6	3	3		8				3	**23**
Waste-water treatment facility						3	2	3		**8**
Total	**9**	**8**	**8**	**4**	**8**	**3**	**5**	**3**	**10**	**58**

5.1.1 Comments on the sampling program

The background control samples chosen were surface water, ground water, soil and sediment. Ground water was chosen because pentaethylenehexamine is a hydrophilic compound and is expected to partition to water, and possibly percholate down to the ground water. The other amines have all high log K_{OW}'s which indicates that they mainly will partition into soil and sediments when discharged into the environment.

Stenungsund was identified as an important point source because the presence of petrochemical industry in the area, where polyethene for plastic products are made.

Roads and traffic are the most common denominator for several of the amines, and therefore sampling close to roads was considered important regarding the discharge and dispersion of the amines from traffic. Air, storm water and soil were sampled. The air samples can be used as indicators of particle wear-off from tyres and asphalt, and the sampling was performed as month-averaged samples in a gradient fashion at two different distances from the road. The soil samples were taken next to the road and at increasing distance from it, in order to enable the assessment of concentration gradient from the source.

The importance of diffusive spreading of the amines was investigated by sampling air, sediment, storm water, surface water and soil, in an urban environment. Since the amines also are used in building materials, it was considered interesting to investigate the wear-off and run-off from such materials to the urban environment as well as the concentrations of the amines in landfills where construction materials may end up in the end of their life cycle.

Measurements have also been conducted in water and sludge from a waste water treatment, STP; facility to see the flux of the amines from domestic use.

Details regarding the samples are shown in *Appendix 1*.

5.2 Regional sampling program

A regional screening programme was carried out by different Swedish county administrative boards and samples were collected and sent to IVL for analysis. A total of 5 county administrative boards participated with a total of 38 samples consisting of 5 influent waters, 10 effluent waters and 10 sludge samples from waste-water treatment plants, along with 12 samples of storm water, and 1 of surface water. Details regarding these samples are shown in *Appendix 2*.

6 Measurements

6.1 Sampling methods

Air samples were collected using a low volume air sampler (LVS) with a flow of approximately 1 m^3/h. The air was passed through a glass fibre filter (MG160, Munktell) where particles were collected and through a glass column packed with polyurethane foam (PUF) adsorbent for the sampling of substances in the gas phase. Filter and adsorbent were changed every week. Prior to sampling, the filters were heated to 400°C and the adsorbent column containing the PUF-adsorbent was cleaned by Soxhlet extraction with acetone (24 h) and metyl-tert-butyl ether (MTBE) for 6 h. After sampling, the filters and columns were wrapped in aluminium foil and sent to the laboratory, where they were stored in a freezer until analysis.

The staff at the different sewage treatment plants (STPs) 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. **Influent** and **effluent waters** were sampled in 1l glass bottles.

Surface **sediment** (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 (-18°C) until analysed. Three sediment samples from the national background lakes were provided from the specimen bank at the Swedish Museum of Natural History.

Surface water samples from background lakes were provided by the Swedish Museum of Natural History (from the very same lakes as were sampled for background sediments). Surface water samples from the city of Stockholm were sampled in glass bottles.

A pooled **surface soil** (0-2 cm) sample from a background area was collected in a glass jar. In a similar fashion soil samples from roadsides were collected. Since all the amines in the study are affiliated to traffic and vehicle related materials, the soil sampling in the vicinity of a major motorway interjunction was conducted in a gradient fashion. At the site soil was sampled at the roadside, as well as at a 200 m-distance from the roadside (in the prevailing wind direction), as well as at a 500 m- distance from the roadside in the prevailing wind direction. As a zero control, a soil sample collected some 100 meters up-wind was also included

Storm water samples, collected during periods of sufficient precipitation to allow sampling, were provided by “Vägverket” and “Gatukontoret”, Stockholm.

Leachate water samples were collected in 1l glass bottles and glass jars.

Groundwater was collected in polyethylene bottles and stored in a freezer (-18°C). Sampling was kindly managed by Lotta Lewin-Pihlblad, Geological Survey of Sweden (SGU).

6.2 Analytical methods

The development of novel work-up and analytical methods for the determination of these amines in environmentally relevant matrices posed a tremendous challenge due to the nature of especially the un-branched, aliphatic amine pentaetylenehexamine, PEHA. The two primary amine groups of pentaetylenehexamine are extremely reactive and basic, rendering the molecule a vast plethora of pKa-values. Performing a QSAR on the protonation behaviour of pentaetylenehexamine it becomes obvious that the molecule will predominately be a polycation at all pH-values below 10 (Chemaxxon QSAR on ChemIDplus website). All six amine groups of the molecule (two primary amines and four secondary amines) can be protonated, thus the molecule might in fact have a vast number of different charge states (and pKa-values).

Pentaetylenehexamine will thus electrostatically interact with solid surfaces of almost all materials (since the net surface charge of solid surfaces is often negative). Therefore, the recovery of spiked solutions and solid samples of pentaetylenehexamine were generally rather low. Glass and sample utensils in the laboratory (as well as solid matrices such as soil, sediment and sludge) will be natural sinks for pentaetylenehexamine and specific deactivation reactions of the surfaces such as silanisation would probably only improve the recovery marginally. Pentaetylenehexamine was thus only being determined in the aqueous samples.

Nevertheless it can be of value to the scientific community involved in occurrence studies of new chemicals to be informed on the analytical methodology that have been tested, evaluated and subsequently being considered less adequate. Results regarding pentaetylenehexamine obtained in this study are therefore regarded as semi-quantitative.

6.2.1 Water sample work-up and pre-concentration of PEHA

The SPE-column (Oasis HLB) was activated prior to use with methanol and ultra-pure water with addition of heptafluorbutyric acid (0.1 %). Pre-filtered water sample, 200-1000 ml depending on sample type, was fortified with heptafluorbutyric acid until acidic reaction and subsequently concentrated on the SPE-column. The cartridge was washed with ultra-pure water and dried for 15 min with the aid of a vacuum pump. The SPE-column was stored in a freezer until HPLC-MS analysis.

Before analysis the SPE-column was eluated with methanol and the extract was concentrated (Turbo Vap II concentration station) with subsequent addition of 1% heptafluorbutyric acid in water.

6.2.2 Water sample work-up and pre-concentration of the aromatic and aliphatic amines

The SPE-column (Oasis HLB) was activated prior to use with methanol and ultra-pure water.

Pre-filtered water sample, 200-1000 ml depending on sample type, was concentrated on the SPE column. The cartridge was washed with ultra-pure water and dried for 15 min with the aid of a vacuum pump. The SPE-column was stored in a freezer until HPLC-MS analysis.

Before analysis the SPE-column was eluated with methanol and the extract was concentrated using a Turbo Vap II concentration station. An aliquot of the extract was prepared for standard addition quantification and analysed with respect to dicyclohexylamine. The rest of the extract was further cleaned by use of SPE and prepared for standard addition quantification of NCBA, IPPD and diphenylamine.

6.2.3 Sludge, soil and sediment sample work up

The solid samples were thawed, added D_6-labeled sulphamethoxazole as internal standard, and extracted as wet sample twice by sonication in a mixture of acetonitril and methanol. The extracts were concentrated using a Turbo Vap II concentration station.

Before analysis the sample extracts were prepared for standard addition quantification and analysed with respect to dicyclohexylamine, NCBA, IPPD and diphenylamine.

Different solvents were tested for extraction of PEHA in soil and sediments, without being able to recover measurable amounts of the spiked PEHA (500 ng) in any samples. In addition, it was not possible to recover PEHA from fortified extracts (500 ng). These findings indicate that PEHA reacts with components of the sample matrix and further makes it difficult to find the free form PEHA in sludge and sediments.

Table 10. Recovery experiments set up for sludge (6584), soil (6679) and sediment (6044) by using methanol/aceonitrile (1:1) in combination with modifiers

Modifier	Sample spiking (500 ng PEHA)	Extract spiking (500 ng PEHA)
Pure solvent	x	x
Water (50 %)	x	x
0.1% formic acid in water (50%)	x	x
0.1% heptafluorobutyric acid (50%)	x	x

6.2.4 Air sample work up.

The air filters were added D_6-labeled sulphamethoxazole as an internal standard, and then extracted twice by sonication in a mixture of acetonitril and methanol. The extract cleaning was performed as for the water samples.

6.2.5 HPLC/MS analysis

Determination of Dicyclohexylamine, NCBA, IPPD, diphenylamine:

Liquid chromatography was performed with an Agilent 1100 liquid chromatography system (Agilent Technologies, Waldbronn, Germany), equipped with an autosampler, a quaternary pump, an on-line degassing system and a diode array detector (UV). The compound separation was performed with a reversed phase C_{18} column (Atlantis dC18, 2.1 mm ID x 150 mm length, 3 µm, Waters, Milford USA). A stainless steel inlet filter (Supelco, 0.8 µm) was used in front of a pre-column with the same stationary phase as the separation columns. Gradient elution was performed with 0.1% formic acid in water as solvent A and 0.1% formic acid in acetonitrile as solvent B. The analytical detector was a Micromass LCT orthogonal-acceleration time-of-flight (TOF) mass spectrometer (MS) equipped with a Z-spray electrospray ion source and a 4 GHz time to digital converter (TDC) (Micromass Ltd., Wythenshawe, Manchester, UK). The instrument was operated in positive mode and the electrospray source parameters were optimised to the following values: sample cone cycling 18/40 V, capillary voltage 3.4 kV, extraction cone 3 V, source temperature 125 °C, desolvation temperature 300 °C, cone gas flow 0 l h^{-1} and desolvation gas flow 600 l h^{-1}. The pusher frequency was operated in automatic mode. The data processing and instrument (HPLC/HRMS) control were performed by the MassLynx software, and quantitation was performed with signal extraction of a peak width of 90 amu (typical).

Determination of PEHA:
The chemical analysis of PEHA were performed with the same equipment as mentioned above. The samples were analysed both with reversed and normal phase chromatography.

Table 11. Molecular Ion Adduct and confirming ions

Compound	$\{M+H\}^+$	Confirming ion	Limits of detection
Dicyclohexylamine	182	100	*
IPPD	184	227	*
NCBA	233	151	*
Diphenylamine	170	116	*
PEHA	233	322	*
D6-Sulphamethoxazole	260	162	

*: Specified for each sample in Appendix 1 and B by using the symbol "<"

7 Results and discussion

Sample list and results from the National and the Regional Screening Programme can be found in appendices A and B, respectively.

7.1 Air

Two of the amines were frequently found in air; NCBA and DCHA.

Both sampling stations in Gothenburg were located in the centre of the city close to heavily trafficated steets. The sampling station at "5:an" is situated on the roof of a 5-floor building and thus representing an urban background whereas the Järntorget sampling station is in the immediate vicinity to the street. NCBA was detected in Gothenburg in five out of six air samples, ranging between 1.8 and 5.0 pg/m^3 (Figure 2). Interestingly, NCBA was also detected in one of the background air samples from Råö, in a concentration of 0.3 pg/m^3. Thus, even though NCBA is unintentionally formed in the production of car tyres, there seems to be a detectable background concentration of this chemical in the Swedish environment.

The other amine found in both urban and background air was dicyclohexylamine (DCHA). DCHA was detected in all six air samples from Gothenburg in concentrations between 23 and 380 pg/m^3 (median 145 pg/m^3). DCHA was also detected in air samples from the Råö background station in concentrations ranging between 26 and 235 pg/m^3 (median 182 pg/m^3) (Figure 3). Thus, it seems as if the concentration of DCHA might in fact be of similar size in background air and in urban air.

The air sampling campaign was conducted in March and April of 2008 and the highest concentrations of NCBA occurred in the end of April. One plausible explanation for this finding may be that the period of use of stubbed tyres generally ends in March-April in Sweden, thus many vehicles may have used stubbed tyres on a relatively dry asphalt turf rendering more particle wear-off compared to the snowy season. For chemicals being dispersed to the environment from tyre material wear-off, the use of stubbed tyres might be of importance in elucidating the emission pathways. It is well known that the use of stubbed tyres increases the PM$_{10}$-fraction of particles in urban air (Vägverket, 2007). The periodicity of sampling is too narrow to establish any seasonal variation and the hypothesis of stubbed tyres would off course need another type of directed sampling program to be fully substantiated.

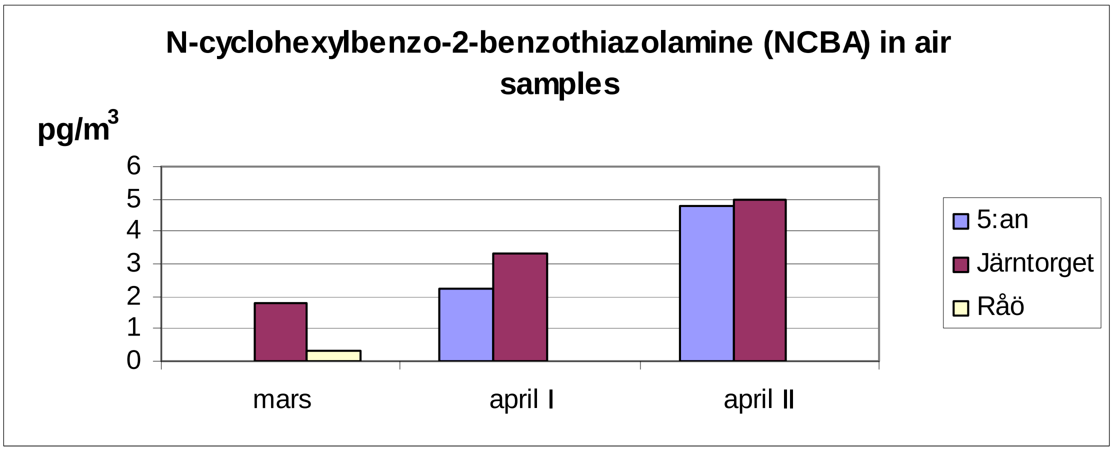


Figure 2. Concentrations of NCBA in urban air sampled in Gothenburg and the background area Råö.

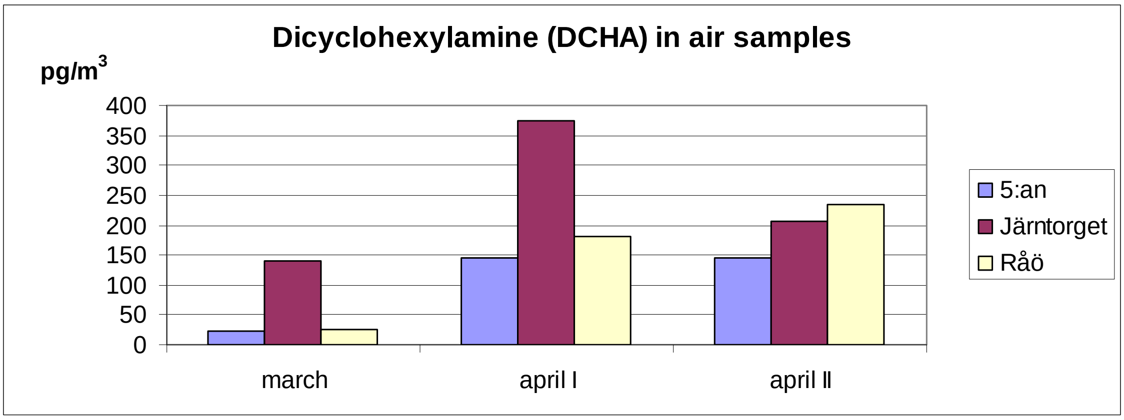


Figure 3. Concentrations of DCHA in urban air sampled in Gothenburg and the background area Råö.

7.2 Surface water

The surface water samples varied considerably in amine contents and to some extent this can be explained by the vastly different nearby sources (petrochemical industry in Stenungsund, typically urban emissions from Stockholm, and in background areas)

Basically none of the amines were detected in surface water from background sites. The most frequently detected amine in surface water was NCBA, which occurred in the surface waters from Stenungsund in two samples out of three (the point source category). Surprisingly, NCBA was not found in surface waters from Stockholm, where the traffic situation is such that wear-off from vehicle tyres is expected to be a major environmental concern in some parts of the city.

Dicyclohexylamine (DCHA) was detected in one of the samples from Stenungsund, while diphenylamine (DPA) was detected in one of the surface water samples from Stockholm (St. Essingen). However, the rather infrequent detection pattern of these substances renders it difficult to draw any conclusions on the dispersive pathway of the amines to surface waters (Figure 4).

IPPD (4-(isopropylamino)-diphenylamine) was not found in any of the eight surface water samples.

The results of the analyses of PEHA, the aliphatic amine, indicted that this substance may occur in the environment. It was detected in the background sample from Bysjön (in Årjäng) at a concentration of 380 ng/l but not in any of the other samples. At this stage, considering the difficulties experienced in establishing an adequate analytical method for PEHA, this result stands out as less reliable. Inconclusive results like theses are sometimes indicative of cross-contamination from laboratory utensils or instrumentation.

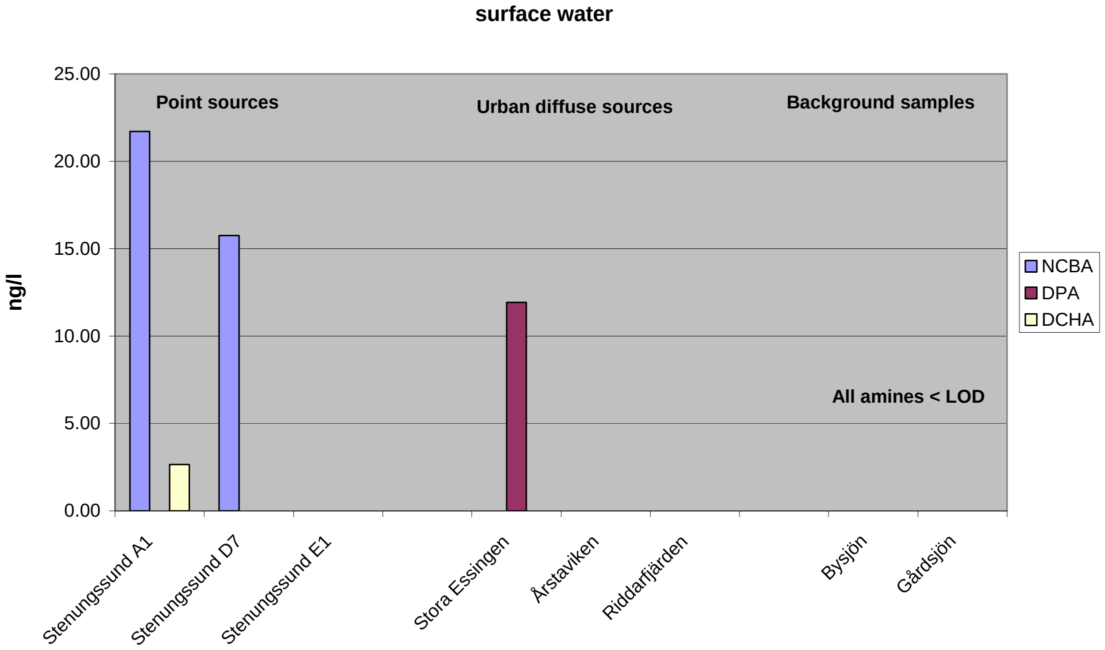


Figure 4. Amines detected in surface waters from various types of sampling locations.

7.3 Ground water

Out of four groundwater samples, one sample (from the sampling station 42:13 in Arjeplog) contained DCHA at a concentration of 4 ng/l. None of the other amines (NCBA, DPA, IPPD) could be detected in any of the groundwater samples.

Regarding PEHA, analysis results indicate that the compound may percholates down to the groundwater yielding concentrations of <5-120 ng/l. The median concentration of PEHA in groundwater (detected in three out of four samples) is 34 ng/l. Unfortunately, these results regarding PEHA seems unrealistic taking into consideration the fact that such a reactive species would probably not easily percholate through 10-15 meters of soil. Also in the case of ground water, incidents of cross-contamination may have occurred.

7.4 Storm water

Dicyclohexylamine (DCHA) occurred in all collected storm water samples but one. The concentrations of DCHA varied tremendously in these samples; <5 – 940 ng/l with a median concentration of 170 ng/l (Figure 5). The highest concentrations of DCHA were found in storm water samples from Stockholm and Trelleborg (the eight highest concentrations out of 20 samples altogether).

NCBA was detected in five out of 20 storm water samples (four samples from urban Stockholm and in one sample from Helsingborg), displaying a concentration range of <1 - 29 ng/l. The median concentration in the Stockholm samples was 7.5 ng/l.

DPA was detected in one sample from Trelleborg (17 ng/l), while IPPD was not detected in any of the samples.

The chemical analysis indicated the presence of PEHA in two storm water samples (from Helsingborg and Malmö) having concentrations of 140 and 110 ng/l respectively.

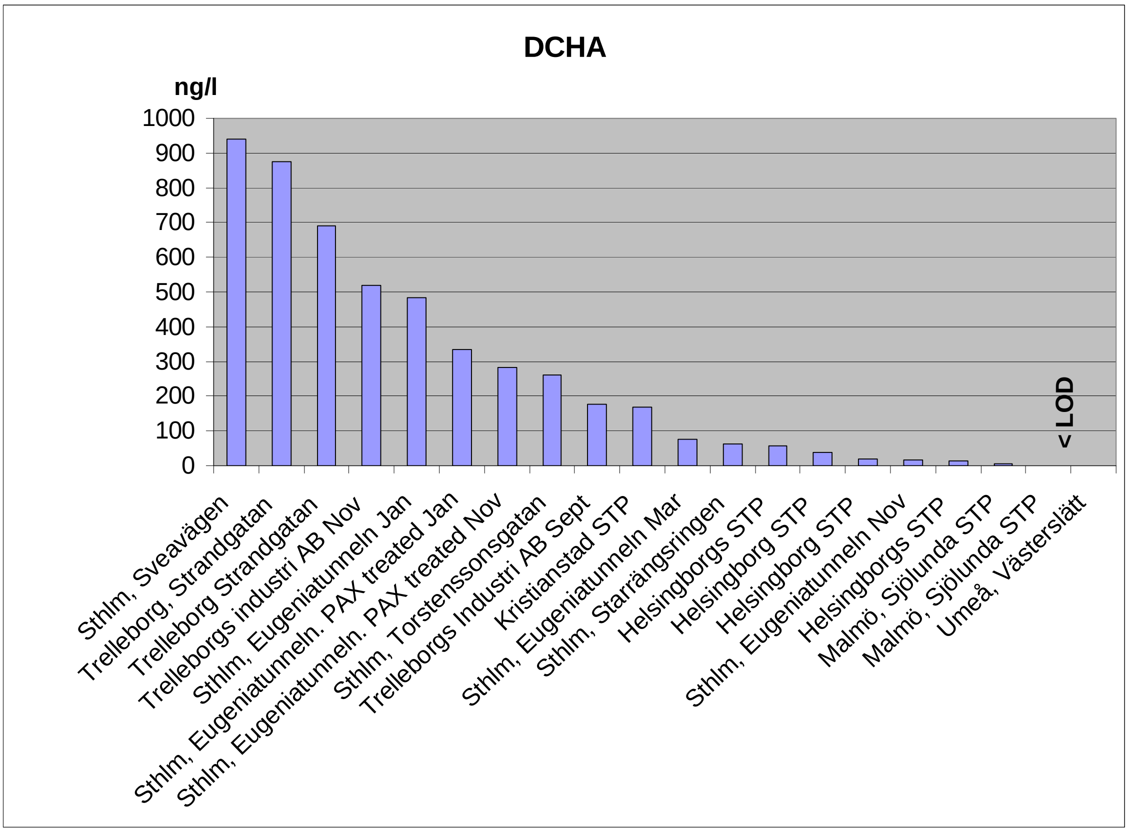


Figure 5. DCHA in storm water samples. LOD of the Västerslätt storm water sample (Umeå) < 6 ng/l.

7.5 Sediment

Also in sediment, DCHA was the most frequently detected amine; found in all eight sediment samples (1-150 ng/g, median concentration 35 ng/g). An interesting aspect of these results is that both the urban sediment samples as well as the background sediments contained higher concentrations than the sediments sampled in the vicinity of a heavily industrialized region (Stenungsund). The sediments from Stenungsund, on the other hand, also contained NCBA and DPA (both amines detected in both samples from Stenungsund) at concentrations of 0.2 ng/g of NCBA and 2-4 ng/g of DPA respectively (Figure 6).

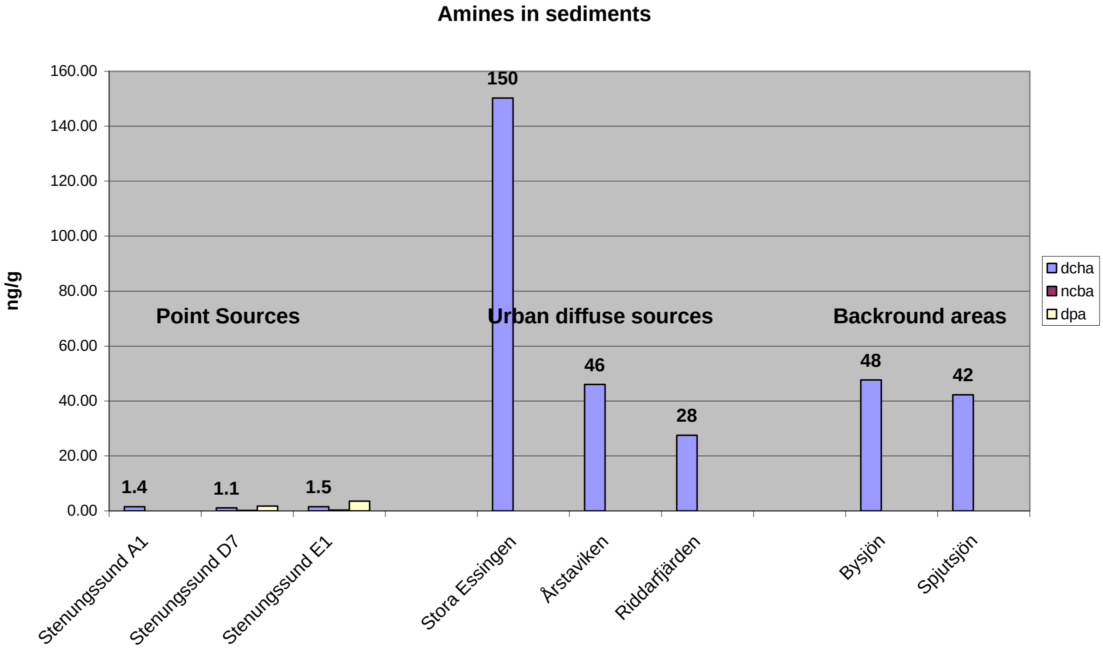


Figure 6. Amines detected in sediment samples from different sampling locations.

7.6 Soil

Dicyclohexylamine (DCHA) was detected in all ten soil samples (1-70 ng/g, median concentration 7 ng/g). Of the other amines included in the study only DPA was detected in only one sample (2 ng/g in a sample from the E4/E20-highway outside Salem, Stockholm).

Since the amines in the study are affiliated to traffic and vehicle related materials, the soil sampling was conducted in a gradient fashion. In an interjunction between the motorways E20 and E4, outside the municipality of Salem in the south of Stockholm, soil was sampled at the roadside. Soil was also sampled at 200 m from the roadside in the prevailing wind direction, as well as at 500 m from the roadside in the prevailing wind direction. As a zero control, a soil sample collected some 100 meters up-wind was also included (see Figure 7). Interestingly, the physical gradient distance is reflected also in the resulting DCHA-concentrations from these samples, possibly corroborating one of the fundamental hypotheses of amine dispersion proposed in this study.

From Figure 8, it is evident that for DCHA, urban diffuse emission seems to be more important than emissions from the expected point source since both the urban soil samples and the road side gradient samples were elevated compared to soil samples from the Stenungsund area.

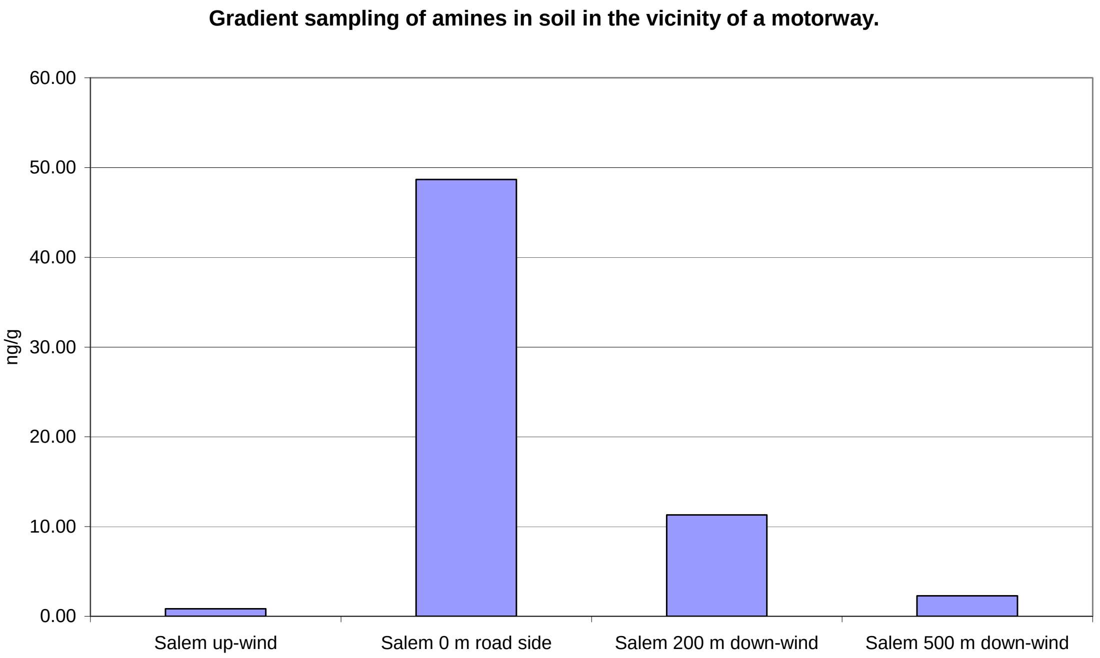


Figure 7. Results of a gradient sampling study with respect to DCHA. The concentrations notably drop off with increasing distance from the road side.

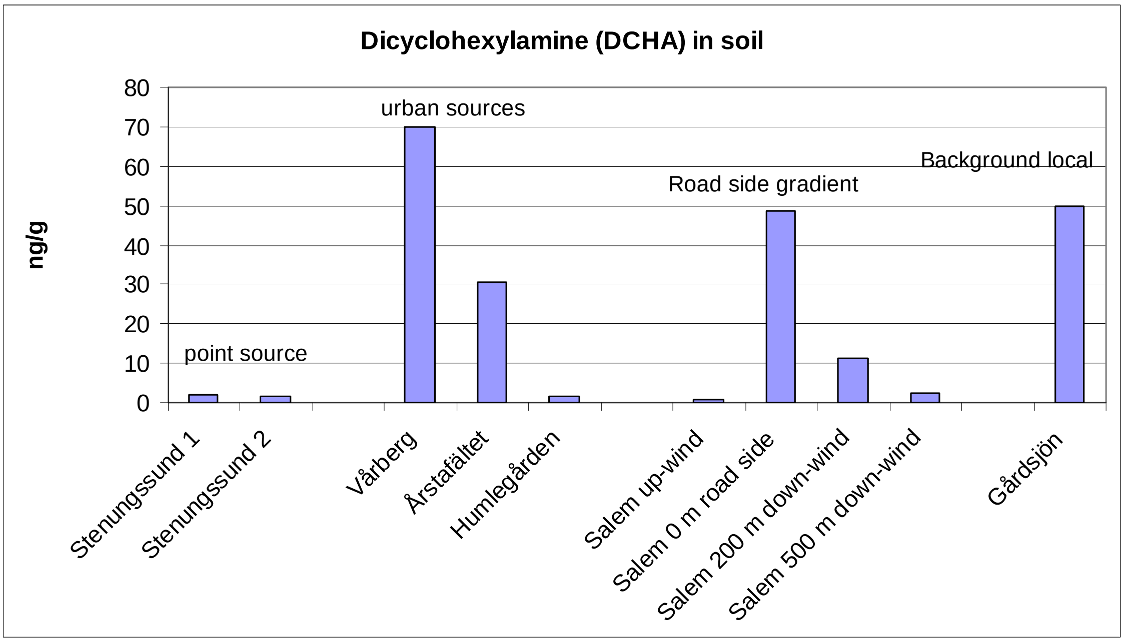


Figure 8. DCHA detected in soil samples from different sampling locations.

7.7 Sewage treatment plants (STP)

7.7.1 Influent water

The only amine found in STP influent water was dicyclohexylamine (DCHA), which was detected in four out of eight influent samples (<11 – 76 ng/l, median 11 ng/l). The influent sample from Kungsängen STP in Västerås stands out as rather elevated compared to the other STPs (Figure 9).

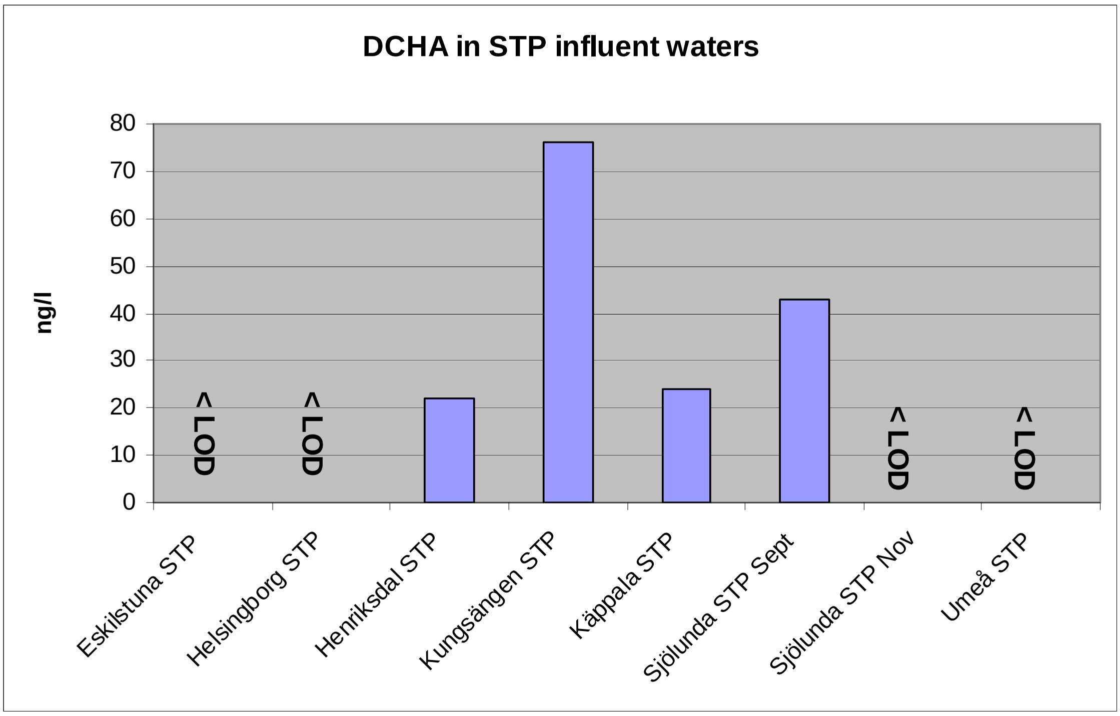


Figure 9. DCHA detected in STP influent water samples. LOD < 11 ng/l in most samples.

7.7.2 Effluent water

Also in STP effluent water streams DCHA was the only amine detected. DCHA was found in seven out of eleven effluent samples in concentrations between <6 and 140 ng/l (median 27 ng/l). The sample having the highest concentration of DCHA was from the largest STP in the study, Henriksdals STP in Stockholm (see Figure 10).

The fact that effluent water streams in general seems to have higher concentrations of DCHA, compared to the STP influent concentrations (see Figure 11) is somewhat puzzling but not unexplainable. Firstly, these samples are not purposely sampled in a flow-proportional manner, thus sampling may reflect the STP influent load variability of DCHA. If DCHA, on the other hand arrives to the STP in a colloidal form (aggregated to suspended solids), and is subsequently being desorbed upon passage of the STP, such concentration profiles may occur.

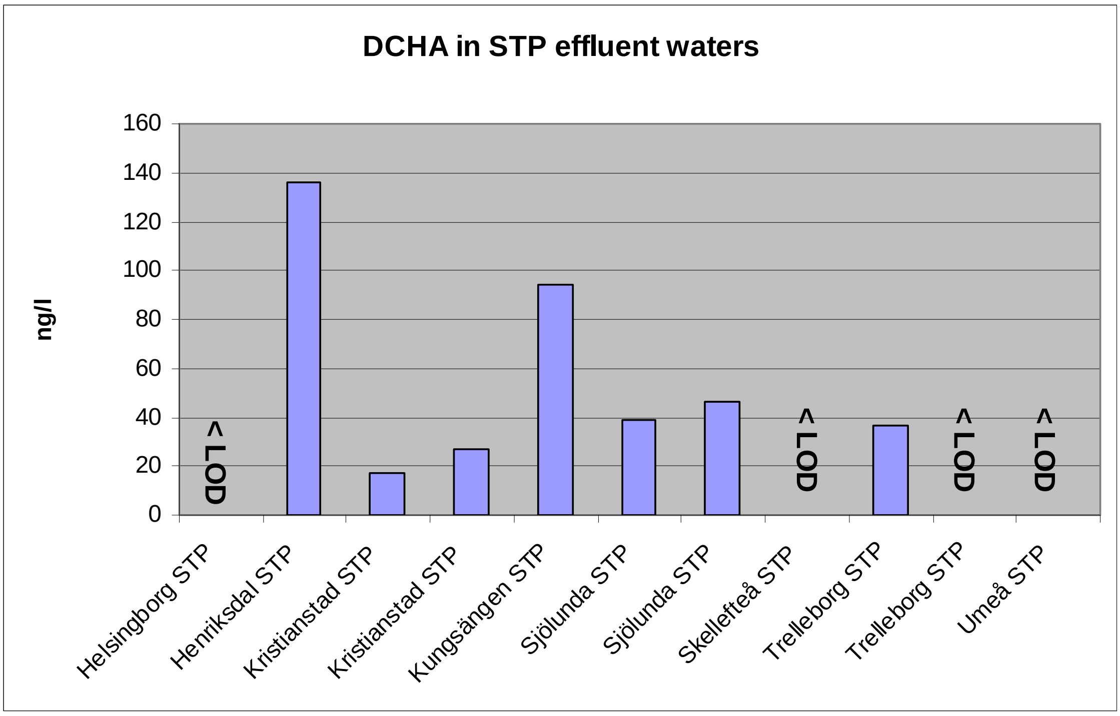


Figure 10. Concentration of DCHA in STP effluent water streams. LOD < 6 ng/l in most samples.

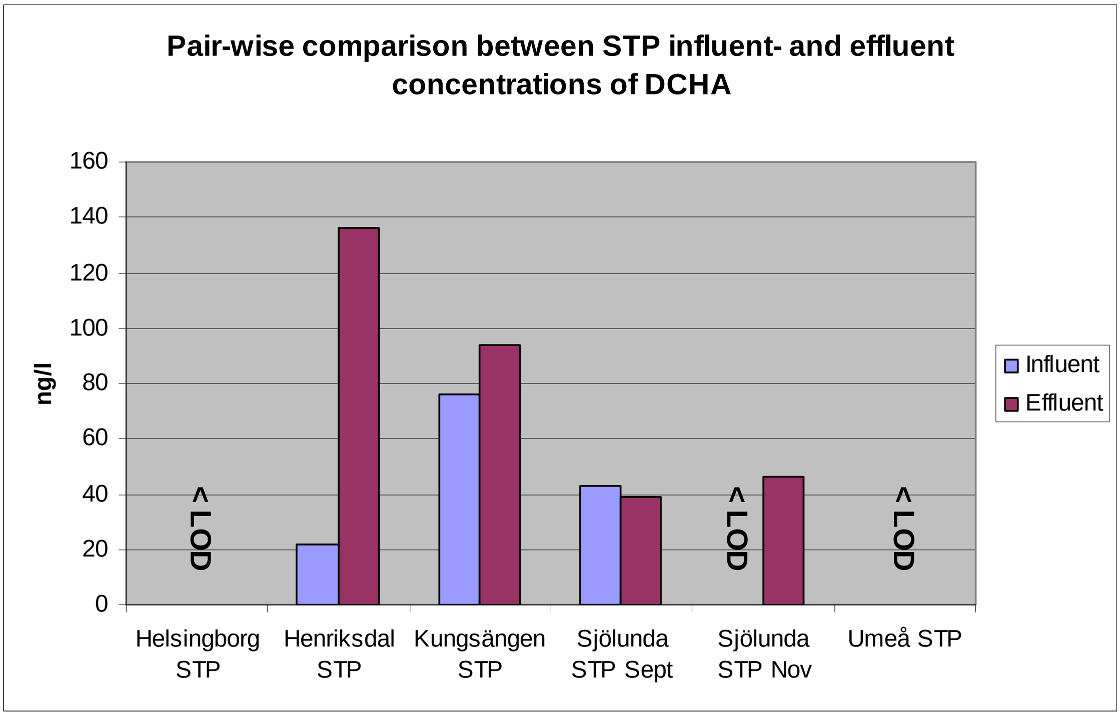


Figure 11. Pair-wise comparison of influent and effluent concentrations in various STPs, with respect to DCHA.

7.7.3 Sludge

The amines detected in sludge reflected the general influent/effluent composition. DCHA was detected in all 13 sludge samples (5-770 ng/g dw, median concentration 90 ng/g dw) (Figure 12).

IPPD were detected in three out of 13 sludge samples (<0.8-3 ng/g dw). IPPD was not detected in any other sample matrix throughout this study. NCBA occurred in one sample out of 13 (Sjölunda STP in Malmö), while diphenylamine (DPA) was not detected at all in sludge which is noteworthy since it is an amine with fairly hydrophobic characteristics (a log Kow-value of 3.5, for instance).

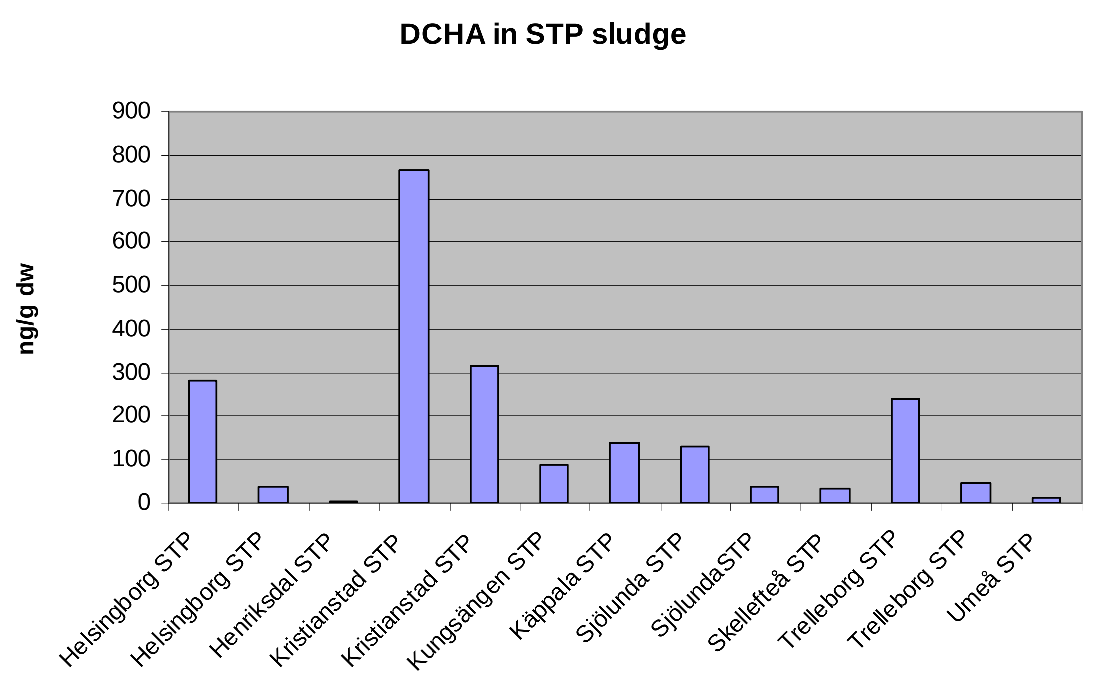


Figure 12. DCHA in STP sludge samples. DCHA was detected in all sludge samples included in the study.

8 Environmental risk assessment

With regard to the very frequently detected compound dicyclohexylamine (DCHA), it is indeed interesting to also assess whether the concentrations reported herein poses any risk to the aquatic environment. This is normally done in a typical MEC/PNEC-approach where MEC is the acronym for measured environmental concentration and PNEC is the acronym for the predicted no effect concentration.

MEC-values in this study include the reported surface water concentrations, as well as the STP effluent concentrations, corrected by a dilution factor. In this particular case the median of the STP effluent concentrations of DCHA is used (27 ng/l, based on seven detected concentrations out of 11 STP effluents being analysed), and this corresponds to a nominal surface water concentration of 2.7 ng/l (dilution factor of ten).

Since there is a vast amount of toxicological data on DCHA, it was decided to utilise the 21 days NOEC of Dapnia magna; 16 µg/l, as a suitable endpoint. Since several endpoints are available for both fish and algae (however only acute data), a safety factor of 100 were chosen. Thus, the resulting PNEC would then correspond to a concentration of 160 ng/l.

The MEC/PNEC would then correspond to a risk quotient of <u>3/160 = 0.019 <<1.</u>

Thus, the surface water concentrations reported herein does not reflect any environmental risks.

However, in some cases the STP effluent water streams may not be diluted a factor of ten when discharged into a recipient if the receiving recipient is relatively small, or if the seasonal variations of the water flow in the tributaries are taken into consideration. Therefore, it would be highly desirable to further extend the measurements of DCHA in Swedish surface waters.

Since DCHA is also being dispersed into the soil and sediment compartments (through air and water respectively), also toxicological endpoints from terrestrial organisms and benthic invertebrates could be suitable in the environmental risk assessment.

9 Conclusions

Several of the amines in this study could be detected in air samples from background locations; a very conclusive finding indicating air transport as an important pathway in the environment.

From this study it can be concluded that dicyclohexylamine (DCHA) is very widely distributed in the Swedish environment; out of 95 samples included in this study DCHA was detected in 78 %.. Furthermore, DCHA was detected in all sampled matrices and practically at all types of sampling locations.

Regarding the other four amines included, NCBA, the vulcanization side-product, was detected in air, storm water and sludge. In samples from the alleged point source Stenungsund, NCBA was as frequently detected as DCHA.

IPPD was detected in three out of 13 sludge samples. Diphenylamine (DPA) was rarely detected and whence the occurrence of DPA was confirmed, the concentrations were close to the detection limit. An exception was observed in one of the surface water samples from Stockholm that contained 12 ng/l of DPA.

In sample matrices typically associated with urban emission scenarios, such as storm waters, STP samples and landfill leachates, DCHA was very frequently detected. However the concentrations of DCHA varied considerably; <5-940 ng/l in storm water, 5-770 ng/g dw in sludge, and <11-1300 ng/l in landfill leachates.

When assessing the environmental risk for DCHA based on the current MEC-data of STP-effluents, a risk quotient << 1 is retrieved. However, this assessment is only concerning aquatic species while DCHA was also detected in soil and sediments. Further measurements are needed to spatially and temporarily estimate median concentrations in surface waters, sediments and soil. Thus in order to properly risk assess DCHA in the environment, extended measurements is needed.

Finally, it can be concluded that the primary hypothesis of this study that traffic, vehicles and their associated materials, were correlated with the emission pathway of the included amines, is partly confirmed. DCHA-emission from traffic to air is as an important emission pathway, as confirmed in the road side gradient study in soil. Regarding DCHA, urban emission seems actually more important than emissions from point sources such as Stenungsund.

The aliphatic amine pentaethylenehexamine (PEHA) proved to be very difficult to analyse and thus, the results concerning that particular compound can only be considered as indicative. Further method development is needed before any conclusions can be drawn regarding the dispersion of PEHA in the Swedish environment.

10 Acknowledgements

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Appendix 1 – National Sample Program, sample details and results

MR	Sample Type	City/Municipality	Site	Matrix	Sampling date	Unit	NCBA	DPA	DCHA	IPPD	PEHA
6985	Background	Göteborg	Råö	air	08-03-11 - 08-04-01	pg/m3	0.3	<4.2	26	<1.1	
6986	Background	Göteborg	Råö	air	08-04-01 - 08-04-15	pg/m3	<0.60	<9.0	182	<2.3	
6987	Background	Göteborg	Råö	air	08-04-15 - 08-04-29	pg/m3	<0.55	<8.2	235	<2.1	
6737	Background	Lerum	SGU Stn 10007:1 Lerum	ground water	2007-11-21	ng/l	<1.2	<19	<5.4	<2.8	9
6734	Background	Hallsberg	SGU Stn 17:10 Hallsberg	ground water	2007-11-12	ng/l	<1.2	<19	<5.4	<2.8	<5
6550	Background	Arjeplog	SGU Stn 42:13 Arjeplog	ground water	2007 nov	ng/l	<1.2	<19	3.9	<2.8	120
6731	Background	Vimmerby	SGU Stn 84:1 Vimmerby	ground water	2007-11-09	ng/l	<1.2	<19	<5.4	<2.8	59
6226	Background	Årjäng	Bysjön	sediment	2007-10-25	ng/g	<0.20	<3.3	48	<0.49	
6227	Background	Falun	Spjutsjön	sediment	2007-11-09	ng/g	<0.32	<5.3	42	<0.78	
6036	Background	Bakgrund	Gårdsjön	soil	2007-09-13	ng/g	<0.57	<9.2	50	<1.4	
6223	Background	Årjäng	Bysjön	surface water	2007-10-03	ng/l	<1.2	<19	<5.4	<2.8	380
6038	Background	Bakgrund	Gårdsjön	surface water	2007-09-13	ng/l	<1.2	<19	<5.4	<2.8	<5
6562	STP	Stockholm	Henriksdal STP	effluent	2007-10-25	ng/l	<2.4	<38	136	<5.6	<5
6892	STP	Umeå	Umeå STP	effluent	2008-03-27	ng/l	<2.3	<37	<11	<5.5	<5
6559	STP	Stockholm	Henriksdal STP	influent	2007-10-25	ng/l	<2.4	<38	22	<5.6	<5
6766	STP	Diffus. ARVLidingö	Käppala STP	influent	2007-02-05	ng/l	<2.3	<37	24	<5.4	<5
6891	STP	Umeå	Umeå STP	influent	2008-03-27	ng/l	<2.3	<37	<11	<5.4	<5
6584	STP	Stockholm	Henriksdal STP	sludge	2007-10-25	ng/g	<0.24	<4.0	5.1	2.2	
6844	STP		Käppala STP	sludge	2007-12-20	ng/g	<0.53	<8.7	139	<1.3	
6896	STP	Umeå	Umeå STP	sludge	2008-04-2	ng/g	<0.32	<5.2	14	<0.76	
6979	Urban	Göteborg	5:an, roof of shopping mall	air	08-03-11 - 08-04-01	pg/m3	<1.2	<17	23	<4.6	
6980	Urban	Göteborg	5:an, roof of shopping mall	air	08-04-01 - 08-04-15	pg/m3	2.2	<12	145	<3.1	
6981	Urban	Göteborg	5:an, roof of shopping mall	air	08-04-15 - 08-04-29	pg/m3	4.8	<12	144	<3.1	
6982	Urban	Göteborg	Järntorget	air	08-03-11 - 08-04-01	pg/m3	1.8	<7.1	140	<1.8	
6983	Urban	Göteborg	Järntorget	air	08-04-01 - 08-04-15	pg/m3	3.3	<14	376	<3.4	
6984	Urban	Göteborg	Järntorget	air	08-04-15 - 08-04-29	pg/m3	5.0	<11	206	<2.7	
6364	Urban	Stockholm	Riddarfjärden	sediment	2007-10-03	ng/g	<0.21	<3.4	28	<0.49	
6358	Urban	Stockholm	Stora Essingen	sediment	2007-10-03	ng/g	<0.27	<4.4	150	<0.64	

MR	Sample Type	City/Municipality	Site	Matrix	Sampling date	Unit	NCBA	DPA	DCHA	IPPD	PEHA
6361	Urban	Stockholm	Årstaviken	sediment	2007-10-03	ng/g	<0.31	<5.0	46	<0.73	
6492	Urban	Stockholm	Humlegården	soil		ng/g	<0.14	<2.3	1.7	<0.33	
6458	Urban	Stockholm	Vårberg	soil		ng/g	<0.20	<3.2	70	<0.47	
6463	Urban	Stockholm	Årstafältet	soil		ng/g	<0.12	<2.0	31	<0.29	
6857	Urban	Stockholm	Eugeniatunneln. PAX treated	storm water	Jan 08	ng/l	<2.4	<38	334	<5.6	<5
6856	Urban	Stockholm	Eugeniatunneln	storm water	Jan 08	ng/l	25	<37	483	<5.5	<5
6889	Urban	Stockholm	Eugeniatunneln	storm water	Mar 08	ng/l	17	<38	77	<5.6	<5
6617	Urban	Stockholm	Eugeniatunneln	storm water	Nov 2007	ng/l	<2.3	<38	16	<5.5	<5
6619	Urban	Stockholm	Eugeniatunneln. PAX treated	storm water	Nov 2007	ng/l	15	<19	282	<2.8	<5
6808	Urban	Stockholm	Starrängsringen	storm water	Nec 2007	ng/l	<2.9	<47	62	<7.0	<5
6807	Urban	Stockholm	Sveavägen	storm water	Dec 2007	ng/l	<2.4	<38	939	<5.6	<5
6806	Urban	Stockholm	Torstenssonsgatan	storm water	Dec 2007	ng/l	29	<48	261	<7.0	<5
6363	Urban	Stockholm	Riddarfjärden	surface water	2007-10-03	ng/l	<1.2	<19	<5.4	<2.8	<5
6357	Urban	Stockholm	Stora Essingen	surface water	2007-12-13	ng/l	<1.2	12	<5.4	<2.8	<5
6360	Urban	Stockholm	Årstaviken	surface water	2008-04-02	ng/l	<1.2	<19	<5.4	<2.8	<5
6540	Point source		Landfill Högbytorp effluent	leachate		ng/l	<0.80	<13	4.2	<1.9	<5
6538	Point source		Landfill Högbytorp influent	leachate		ng/l	<2.9	<47	1274	<6.9	<5
6395	Point source		Löt Sewage Treat. Plant first dam surface water	leachate		ng/l	<2.3	<37	<11	<5.4	
6042	Point source	Stenungsund	Stenungssund A1	sediment	2007-09-13	ng/g	<0.14	<2.3	1.4	<0.33	
6044	Point source	Stenungsund	Stenungssund D7	sediment		ng/g	0.17	1.8	1.1	<0.27	
6046	Point source	Stenungsund	Stenungssund E1	sediment	2007-10-03	ng/g	0.28	3.6	1.5	<0.45	
6677	Point source		E4/E20 Salem 0 m down-wind	soil		ng/g	<0.15	<2.5	49	<0.36	
6678	Point source		E4/E20 Salem 200 m down-wind	soil		ng/g	<0.12	2.2	11	<0.29	
6679	Point source		E4/E20 Salem 500 m i down-wind	soil		ng/g	<0.09	<1.6	2.3	<0.22	
6676	Point source		E4/E20 Salem Zero-sample up-wind	soil		ng/g	<0.16	<2.6	0.86	<0.38	
6040	Point source	Stenungsund	Stenungssund	soil	2007-09-13	ng/g	<0.25	<4.0	2.0	<0.59	
6041	Point source	Stenungsund	Stenungssund	soil	2007-09-13	ng/g	<0.23	<3.7	1.8	<0.54	
6043	Point source	Stenungsund	Stenungssund A1	surface water	2007-10-03	ng/l	22	<19	2.7	<1.2	<5
6045	Point source	Stenungsund	Stenungssund D7	surface water	2007-10-03	ng/l	16	<19	<5.4	<2.8	<5
6047	Point source	Stenungsund	Stenungssund E1	surface water	2007-10-03	ng/l	<1.2	<19	<5.4	<2.8	<5

Appendix 2 – Regional Sample Program, sample details and results

MR	County	Municipality	Site	Matrix	Sampling date	Unit	NCBA	DPA	DCHA	IPPD	PEHA
6597	Skåne (M)	Helsingborg	Helsingborg STP	effluent	2007-10-29--11-04	ng/l	<1.2	<19	<5.4	<2.8	<5
6100	Skåne (M)	Helsingborg	Helsingborg STP	influent	2007-09-17	ng/l	<2.3	<37	<11	<5.4	<5
6103	Skåne (M)	Helsingborg	Helsingborg STP	sludge	2007-09-17	ng/g	<0.48	<7.8	282	<1.2	
6598	Skåne (M)	Helsingborg	Helsingborg STP	sludge	2007-10-29--11-04	ng/g	<0.40	<6.5	39	<0.95	
6717	Skåne (M)	Helsingborg	Helsingborg STP	storm water	2007-11-16	ng/l	<1.2	<19	20	<2.8	<5
6718	Skåne (M)	Helsingborg	Helsingborg STP	storm water	2007-11-16	ng/l	4.8	<19	37	<2.8	<5
6366	Skåne (M)	Helsingborg	Helsingborgs STP	storm water	2007-09-21	ng/l	<1.2	<19	13	<2.8	<5
6367	Skåne (M)	Helsingborg	Helsingborgs STP	storm water	2007-09-21	ng/l	<1.2	<19	56	<2.8	140
6140	Skåne (M)	Kristianstad	Kristianstad STP	effluent	2007-09-11--09-17	ng/l	<2.3	<37	17	<5.4	<5
6687	Skåne (M)	Kristianstad	Kristianstad STP	effluent	2007-11-05	ng/l	<2.4	<38	27	<5.6	<5
6141	Skåne (M)	Kristianstad	Kristianstad STP	sludge	2007-09-11--09-17	ng/g	<0.43	<7.0	766	<1.1	
6685	Skåne (M)	Kristianstad	Kristianstad STP	sludge	2007-11-05	ng/g	<0.46	<7.6	316	<1.2	
6143	Skåne (M)	Kristianstad	Kristianstad STP	storm water	2007-09-11--09-17	ng/l	<2.3	<37	169	<5.4	<5
6124	Skåne (M)	Malmö	Sjölunda STP	effluent	2007-09-13	ng/l	<2.3	<38	39	<5.6	<5
6607	Skåne (M)	Malmö	Sjölunda STP	effluent	2007-11-01	ng/l	<2.3	<38	46	<5.5	<5
6122	Skåne (M)	Malmö	Sjölunda STP	influent	2007-09-13	ng/l	<2.3	<38	43	<5.5	<5
6605	Skåne (M)	Malmö	Sjölunda STP	influent	2007-11-01	ng/l	<2.3	<37	<11	<5.5	<5
6609	Skåne (M)	Malmö	Sjölunda STP	sludge	2007-11-01	ng/g	<0.41	<7.0	130	2.5	
6129	Skåne (M)	Malmö	Sjölunda STP	storm water	2007-09-13	ng/l	<2.3	<38	6.4	<5.5	110
6130	Skåne (M)	Malmö	Sjölunda STP	storm water	2007-09-13	ng/l	<1.5	<24	<6.7	<3.5	<5
6126	Skåne (M)	Malmö	SjölundaSTP	sludge	2007-09-13	ng/g	0.69	<6.6	38	<0.97	
6171	Skåne (M)	Trelleborg	Strandgatan OK Q8	storm water	2007-09-25	ng/l	<2.4	<38	876	<5.6	<5
6708	Skåne (M)	Trelleborg	Strandgatan OK Q8	storm water	2007-11-20	ng/l	<1.5	17	691	<3.6	<5
6169	Skåne (M)	Trelleborg	Trelleborg STP	effluent	2007-09-25	ng/l	<2.3	<37	37	<5.4	<5
6704	Skåne (M)	Trelleborg	Trelleborg STP	effluent	2007-11-20	ng/l	<2.4	<38	<11	<5.6	310
6173	Skåne (M)	Trelleborg	Trelleborg STP	sludge	2007-09-25	ng/g	<0.46	<7.4	239	2.8	
6703	Skåne (M)	Trelleborg	Trelleborg STP	sludge	2007-11-20	ng/g	<0.60	<9.7	48	<1.5	
6709	Skåne (M)	Trelleborg	Trelleborgs industri AB	storm water	2007-11-20	ng/l	<1.2	<20	518	<2.9	<5

MR	County	Municipality	Site	Matrix	Sampling date	Unit	NCBA	DPA	DCHA	IPPD	PEHA
6170	Skåne (M)	Trelleborg	Trelleborgs Industri AB	storm water	2007-09-25	ng/l	<2.3	<37	176	<5.5	<5
6270	Södermanland (D)	Eskilstuna	Eskilstuna STP	influent	2007-09-17 - 21	ng/l	<2.3	<38	<11	<5.5	<5
6848	Västerbotten (AC)	Skellefteå	Skellefteå STP	effluent	2008-01-15	ng/l	<2.3	<37	<11	<5.5	<5
6849	Västerbotten (AC)	Skellefteå	Skellefteå STP	sludge	2008-01-15	ng/g	<0.57	<9.2	34	<1.4	
6716	Västerbotten (AC)	Umeå	Västerslätt	storm water	2007-11-21	ng/l	<1.2	<19	<5.4	<2.8	<5
6599	Västernorrland (Y)	Sundsvall	Ljusta bäcken	surface water	2007-11-06	ng/l	10	<19	41	<2.8	<5
6371	Västmanland (U)	Västerås	Kungsängen STP	effluent	2007-10-03	ng/l	<2.3	<38	94	<5.5	<5
6370	Västmanland (U)	Västerås	Kungsängen STP	influent	2007-10-03	ng/l	<2.3	<37	76	<5.5	<5
6375	Västmanland (U)	Västerås	Kungsängen STP	sludge	2007-10-03	ng/g	<0.48	<7.9	87	<1.2	