

Results from the Swedish National Screening Programme 2006

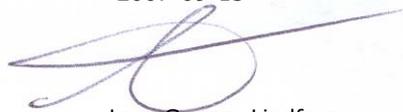
Subreport 1: Phthalates

Anna Palm Cousins, Mikael Remberger, Lennart Kaj,
Ylva Ekheden, Brita Dusan, Eva Brorström-Lundén

B1750

June 2007

This report approved
2007-09-13



Lars-Gunnar Lindfors
Scientific Director

Sammanfattning

IVL har på uppdrag av Naturvårdsverket genomfört en screening av ftalater. De två substanser som ursprungligen ingick i studien var di-isononylftalat (DINP) och di-isodecylftalat (DIDP). Dessa är de två ftalater som är vanligast förekommande som mjukgörare i EU idag. De är högmolekylära och har relativt hög persistens och antas vara ganska orörliga i miljön. Som grupp hör dock inte ftalater till de mest långlivade kemikalierna. Vissa studier indikerar även carcinogena effekter av DINP, men det är inte helt klarlagt.

Tillsammans med di-n-oktylftalat (DNOP) får DINP och DIDP inte förekomma i barnleksaker som kan stoppas i munnen i halter över 0.1 % (summan av de tre).

Utöver DINP och DIDP inkluderades även di-(2-etyl)hexylftalat (DEHP) som jämförelsesubstans. Denna var tidigare den mest använda ftalaten men har till stor del ersatts av de två förstnämnda. Även adipaten di-(2-ethyl)hexyladipat (DEHA) inkluderades i mätningarna. Denna ingick i ett tidigare screeningprogram (Remberger et al., 2005) och är en mjukgörare som i många fall ersatt DEHP. I luftproverna analyserades ytterligare fyra ftalater; di-etylftalat (DEP), di-*iso*-butylftalat (DIBP), di-n-butylftalat (DBP) samt butylbensylftalat (BBzP), då dessa ämnen tidigare bestämts i luftprover och analysmetoden fanns utvecklad.

Det huvudsakliga syftet med föreliggande screeningstudie var att bestämma koncentrationer av ftalater i olika matriser i miljön, att belysa viktiga transportvägar samt att bedöma sannolikheten för pågående emissioner i Sverige. Ytterligare syften var att utreda förekomsten av atmosfärisk transport samt upptag i biota och i människor. En provtagningsstrategi utarbetades utifrån en kartläggning om möjliga källor. Utifrån denna valdes provplatser som representerade punktkällor, diffusa källor (reningsverk, urban miljö) samt bakgrundsområden. För att kartlägga mänsklig exponering insamlades livsmedel samt urinprover. Totalt bestämdes ftalater i 66 prover av luft, sediment, slam, fisk, livsmedel samt urin.

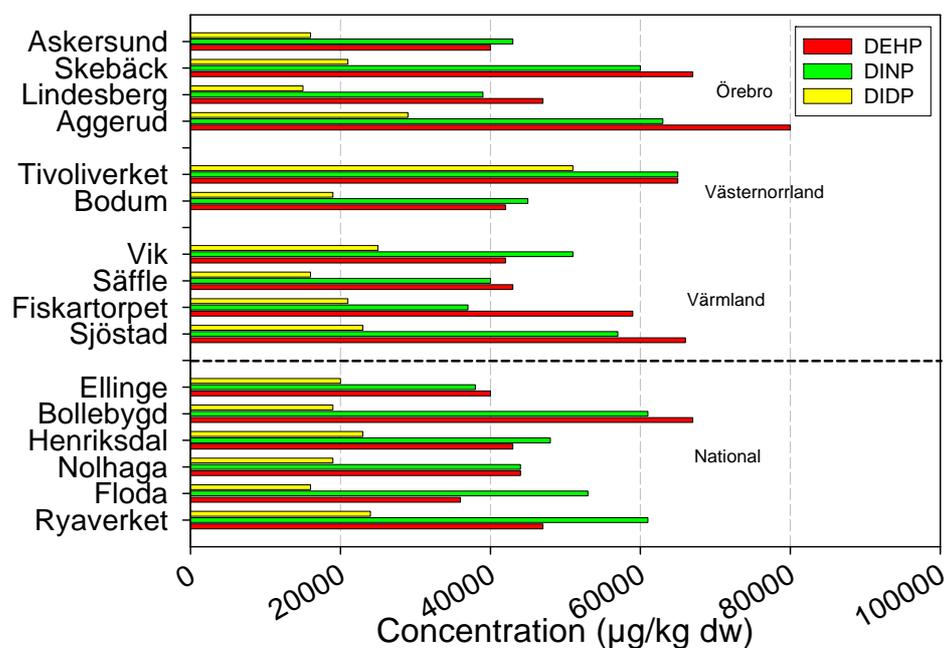
11 av dessa 66 prover utgjordes av regionala prover (10 slamprover samt ett sedimentprov) som skickats in från tre deltagande länsstyrelser. Urvalet av regionala prover baserades på olika strategier, de utgör antingen ett komplement till andra regionala övervakningsprogram, eller kommer ifrån lokala misstänkta punktkällor. De flesta regionala prover kom från kommunala reningsverk, med syfte att få en uppfattning om den diffusa belastningen i länet

Nedan visas en tabell med uppmätta halter i olika matriser. Denna tabell inkluderar även de 11 prover som insamlats regionalt.

	Luft (ng/m ³)	Sediment (µg/kg TS)	Slam (mg/kg TS)	Biota (µg/kg färskvikt)	Livsmedel (µg/kg färskvikt)	Urin* (µg/L)
Antal prov	12	13	16	12	6	6
DEHP	0.5-3	82-2800	36-80	15-26	140-1900	0.7-11
DF (%)	100	69	100	33	100	100
DINP	0.3-1.1	130-3200	37-65	<50	54-260	
DF (%)	83	62	100	0	67	<50
DIDP	0.3-5.5	190-3400	15-51	<50	21-32	DF: 0 %
DF (%)	67	62	100	0	33	
DEHA	0.02-0.6	68-520	0.11-0.18	5-23	8.2-470	n.c.
DF (%)	92	38	13	17	100	
DEP	0.05-1.2	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	92					
DIBP	0.15-2.6	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					
DBP	0.08-15	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					
BBzP	0.02-0.17	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					

*I urin analyserades metaboliterna MEHP samt summan (MINP+MIDP)
n.c.= "not commissioned", dvs ingick ej i uppdraget. DF=Detektionsfrekvens

Figuren nedan visar de uppmätta halterna i de regionala slamproven, samt de slamprover som analyserats i det nationella programmet. Sedimentprovet från Strandmossens deponi i Kristinehamn, Värmland uppvisade halter motsvarande 400, 440 samt 290 µg/kg TS för DEHP, DINP respektive DIDP.



DEHP var den substans som oftast detekterades. Iso-ftalaterna återfanns i samtliga slamprover, men de återfanns också i de flesta andra matriser med undantag för urin och biota.

Mätningarna indikerar tydligt att *iso*-ftalater släpps ut i den svenska miljön idag. Låga halter av ftalater förekom generellt i prover insamlade i bakgrundsområdena varför långväga atmosfärisk transport av ftalater inte torde vara något stort problem.

Halterna i luft av *iso*-ftalater är fortfarande i allmänhet något lägre än halterna av DEHP, med undantag av urban luft, där DIDP dominerar. Vad detta beror på är oklart, eftersom användningen av DIDP är cirka hälften så stor som användningen av DINP, och den är inte heller mer flyktig än DINP. Vi rekommenderar därför ytterligare mätningar av *iso*-ftalater i urban luft och möjligen i anslutning till punktkällor, för att vidare utreda frågan.

I sediment och slam är nivåerna av DINP i samma storleksordning eller högre än DEHP. För sediment gäller detta även för DIDP, medan denna i slam motsvarar ca 50 % av uppmätta halter av DEHP.

Upptag av *iso*-ftalater i biota tycks vara begränsat, då de ej återfunnits i fisk.

Den relativa fördelningen av ftalathalter i miljön tycks reflektera konsumtionsmönstret för ca 5 år sedan – vilket indikerar en tidsförskjutning som kan förklaras av att stora mängder DEHP trots den minskade användningen fortfarande finns lagrade i teknosfären och ger upphov till sekundära emissioner.

Monoestrar av *iso*-ftalater kunde inte detekteras i urin, vilket indikerar en låg human exponering. På grund av den relativt höga detektionsgränsen (50 µg/l) går det inte att jämföra denna exponering med exempelvis exponering för DEHP. Halterna av *iso*-ftalater i livsmedel är lägre än halterna av DEHP vilket tyder på lägre exponering genom föda. Det finns dock betydligt fler exponeringsvägar som kan vara av betydelse, exempelvis inandning av inomhusluft vilket inte ingick i denna undersökning.

Eftersom det inte finns några bestämda risknivåer (PNEC-värden) och då toxicitetsdata gällande *iso*-ftalater är motsägelsefulla är det inte möjligt att göra någon riskbedömning avseende dessa ämnens förekomst i miljön.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of selected phthalates. The overall objectives of the screening were to determine the concentrations of the substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport and uptake in biota and humans. The screening programme included measurements in background areas and in the vicinity of potential point sources. Measurements were also carried out in urban areas reflecting diffuse emission pathways from the society. Sample types were air, sediment, sludge, biota (fish), foodstuffs and human urine. A total of 66 samples were included.

The phthalates included in the study were di-(2-ethyl)hexyl phthalate (DEHP), di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP) and di-(2-ethyl)hexyl adipate (DEHA). In air, four additional substances were determined. These were di-ethyl phthalate (DEP), di-*iso*-butylphthalate (DIBP), di-*n*-butyl phthalate (DBP) and butylbenzyl phthalate (BBzP).

The table below shows the detected concentration ranges of phthalates in various matrices.

Substance	Air (ng/m ³)	Sediment (µg/kg dw)	Sludge (mg/kg dw)	Biota (µg/kg FW)	Foodstuffs (µg/kg FW)	Urine* (µg/L)
# of samples	12	13	16	12	6	6
DEHP	0.5-3	82-2800	36-80	15-26	140-1900	0.7-11
DF (%)	100	69	100	33	100	100
DINP	0.3-1.1	130-3200	37-65	<50	54-260	
DF (%)	83	62	100	0	67	<50
DIDP	0.3-5.5	190-3400	15-51	<50	21-32	DF: 0 %
DF (%)	67	62	100	0	33	
DEHA	0.02-0.6	68-520	0.11-0.18	5-23	8.2-470	n.c.
DF (%)	92	38	13	17	100	
DEP	0.05-1.2	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	92					
DIBP	0.15-2.6	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					
DBP	0.08-15	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					
BBzP	0.02-0.17	n.c.	n.c.	n.c.	n.c.	n.c.
DF (%)	100					

*In urine, the metabolites MEHP and sum (MINP/MIDP) were analysed.
n.c.=not commissioned. DF = Detection frequency

DEHP was the most commonly detected substance. The iso-phthalates were detected in all sludge samples, and they were also found in most other matrices apart from human urine and biota.

The measurements clearly show that there are on-going emissions of *iso*-phthalates to the Swedish environment.

In general, background sites were fairly non-contaminated, and long-range atmospheric transport does not seem to be of major importance for these substances, even though in particular DEHP has the potential to reach background areas.

The atmospheric levels of *iso*-phthalates are generally slightly lower than DEHP levels with the exception of urban air, where DIDP is the dominant species. We recommend additional measurements of *iso*-phthalates in urban air and possibly also air close to industrial facilities, in order to further investigate the high levels of DIDP.

In sediments and sludge levels of DINP were found to be in similar order of magnitude as or even higher than the levels of DEHP. In sediments this was true also for DIDP, whereas DIDP levels in sludge correspond to about 50 % of the DEHP levels.

Uptake of phthalates in biota seems to be limited, as they have not been found in fish, apart from a few samples.

The concentrations of *iso*-phthalate monoesters in human urine possibly indicate a low human exposure but the high LOD (50 µg/l) does not allow a direct comparison with *e.g.* MEHP. The levels of *iso*-phthalates in food-stuffs are generally lower than the levels of DEHP, indicating limited exposure from food. There are, however, other possible exposure routes, which may be of importance, *e.g.* inhalation of indoor air.

The current pattern of environmental levels seems to mirror the consumption pattern roughly five years ago – thus reflecting a time lag which may be explained by the large amounts of DEHP still present in the technosphere despite a decrease in use.

As there are no set risk levels of *iso*-phthalates, and ambiguous data on toxicity, it is not possible to determine the risk of their presence in the environment.

Table of contents

1	Introduction.....	7
2	Chemical properties, fate and toxicity.....	8
2.1	Properties and fate.....	8
2.2	Toxicity.....	10
2.3	Human exposure and metabolism.....	11
3	Production, consumption, emissions and regulation.....	11
3.1	Emissions.....	13
3.2	National and EU legislation on phthalates.....	13
4	Previous measurements in the environment.....	14
5	Sampling strategy and study sites.....	14
5.1	National.....	14
5.2	Regional.....	15
6	Methods.....	16
6.1	Sampling.....	16
6.2	Analysis.....	16
7	Results and discussion.....	19
7.1	Air.....	19
7.2	Sediments.....	22
7.3	Biota.....	24
7.4	Sludge.....	24
7.5	Foodstuffs.....	25
7.6	Urine.....	26
8	Conclusions.....	27
9	Acknowledgements.....	27
10	References.....	28

Appendix. Information on samples and lists of results

1 Introduction

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of phthalates, 1,5,9-cyclododecatriene, zinc pyrithione, pharmaceuticals and chromium(VI). These substances are emitted and distributed in the environment via a variety of sources, e.g. point sources and via use in consumer products. Pharmaceuticals in particular are frequently spread by domestic use.

The overall objectives of the screening were to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport (phthalates, 1,5,9-cyclododecatriene and chromium) and uptake in biota.

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

Table 1. Substances / substance groups included in the screening

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

This sub-report considers the screening of phthalates.

The phthalates included in this study were di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), which are the two substances that account for the majority of the phthalates used as plasticisers in the EU today. The di-(2-ethyl)hexyl phthalate (DEHP) was included as a reference, since it until recently was the major phthalate of use in the region and it has previously been included in several investigations. In addition, the adipate di-(2-ethyl)hexyl adipate (DEHA) was included for comparative reasons. This substance was included in a previous screening study (Remberger et al., 2005).

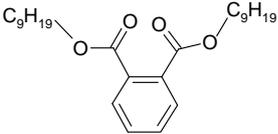
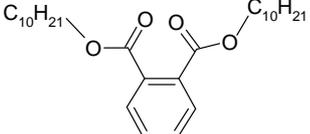
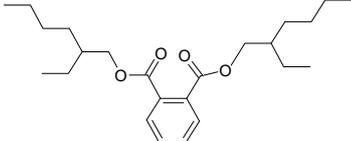
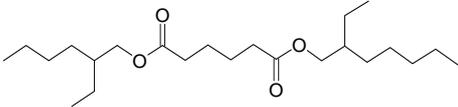
Four additional phthalates were analysed in the air samples, namely di-ethyl phthalate (DEP), di-*iso*-butylphthalate (DIBP), di-*n*-butylphthalate (DBP) and butylbenzyl phthalate (BBzP).

2 Chemical properties, fate and toxicity

2.1 Properties and fate

Phthalate esters are colourless, odourless liquids, belonging to a group of organic chemicals produced from oil by esterification of alcohols. For di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) this procedure is undertaken by reaction with “oxo” alcohols of chain length nine and ten, which in turn are produced through carbonylation of an alkene. The varying position of the C=C double bond in the alkene and the varying effectiveness of catalysts used in the reaction generates a mixture of differently branched alcohols and consequently also of phthalates, hence the term “iso”-phthalates (Plasticisers Information Centre, 2007). Di-2-ethylhexyl phthalate (DEHP) is the phthalate ester of the alcohol 2-ethyl hexanol, which is generally produced by dimerisation of butyraldehyde, which is synthesized from propylene. Thus, the manufacturing processes vary for the different phthalates, and DEHP represents a single substance. In addition to the phthalates, the corresponding adipate of DEHP has been included in the current study, di-2-ethylhexyl adipate (DEHA), formed through esterification of adipic acid with 2-ethyl hexanol. Table 2 shows the molecular structure of the substances included.

Table 2. Names, molecular structures and CAS-numbers of chemicals included in the study

Di-isononyl-phthalate (DINP)	68515-48-0 28553-12-0	
Di-isodecyl-phthalate (DIDP)	68515-49-1 26761-40-0	
Di(2-ethylhexyl) phthalate (DEHP)	117-81-7	
Di(2-ethylhexyl) adipate (DEHA)	103-23-1	

As evident from Table 2, DINP and DIDP are both registered under two different CAS-numbers. These represent different methods in the production of the iso-alcohol used in the synthesis of the phthalate. The alcohol is produced either via the dimerisation of butene or the oligomerisation of propylene/butene, and the resulting products are assigned different CAS-numbers. Table 3 summarises the physico-chemical properties of the same compounds.

Table 3. Physico-chemical properties of chemicals included in the study

Property	DINP ^a	DIDP ^a	DEHP ^a	DEHA ^d
MW (g/mol)	418.6	446.7	390.6	370.6
Melting point (°C)	-48	-46	-46	-68
Boiling point (°C)	>400 ^b	>400 ^b	230 ^b	417
Vapour pressure (Pa)	6.8×10^{-6}	1.84×10^{-6}	3.4×10^{-2}	1.1×10^{-4}
Water solubility (mg/L)	3.08×10^{-4}	3.81×10^{-5}	2.49×10^{-3}	0.78
Henry's Law constant (Pa×m ³ /mol)	9.26	21.6	3.95	0.044
Log Kow	8.6	9.46	7.73	>6.1
Half-lives t_{1/2} (h)				
Air	17	17	17	17
Water	550	550	550	170
Soil	5500	5500	5500	550
Sediment	5500	5500	5500	1700

^aCousins et al. 2003 ^bEU RA, ^cSRC database ^dRemberger et al., 2005

The physico-chemical properties indicate that the iso-phthalates and DEHA may exist both in the particle phase and the vapour phase of the atmosphere, whereas DEHP to a larger extent is expected to be found in the vapour phase. All the chemicals have low water solubilities and high log K_{OW} values, which shows their preference to partition to lipids or organic carbon-containing phases in the environment.

A fate modelling exercise was performed for DINP and DIDP using the evaluative fate model EQC (Equilibrium Criterion Model; Mackay et al., 1996), yielding results according to Table 4. The results from previous evaluative modelling efforts of DEHP by Cousins et al. (2003) and of DEHA by Remberger et al. (2005) have also been included in the table.

The numbers in the table should be regarded as indicative, as they are dependent on model structure as well as chemical property data. However, overall, the modelling results confirm that soils and sediments are the primary receiving media both for phthalates and DEHA, but that DEHA has a higher tendency to partition to the aquatic phase, which is in accordance with its higher water solubility and lower logK_{ow}-value. Table 4 also shows that these three phthalates have similar partitioning behaviour and predicted residence times in the system, with the overall residence time differing only by a few days. DEHA is predicted to have a system residence time which is a factor of 5 to 12 lower than the phthalate group, depending on emission medium.

Relative to DEHA, phthalates are thus predicted to be more stable in the environment and more resistant to degradation. Cousins et al (2003) previously stated that phthalates as a group is not considered "very" persistent but that individual phthalates of higher molecular weight, such as the ones included in the current study, have higher environmental stability. Despite this fact, Cousins et al. concluded that the relative "stickiness" of these phthalates and their tendency to partition to soils, sediments and aerosols will reduce their mobility and bioavailability in the environment.

Table 4. Results from EQC modelling of phthalates and DEHA, using emission rates of 1000 kg/h.

Chemical	Emission medium	Percent at steady state				Residence time (d)
		Air	Water	Soil	Sediment	
DINP ^a	Air	0.46	0.21	94	5.8	114
	Water	<0.1	3.5	<0.1	97	190
	Soil	<0.1	<0.1	>99	<0.1	331
	All three	<0.1	1.1	69	30	211
DIDP ^a	Air	0.44	0.21	94	5.8	117
	Water	<0.1	3.5	<0.1	97	190
	Soil	<0.1	<0.1	>99	<0.1	331
	All three	<0.1	1.1	69	30	213
DEHP ^b	Air	0.5	0.2	93	5.9	100
	Water	<0.1	3.9	<0.1	96	190
	Soil	<0.1	<0.1	>99	<0.1	330
	All three	<0.1	1.1	69	30	210
DEHA ^c	Air	6	2	83	9	9.3
	Water	<0.1	17	<0.1	83	34
	Soil	<0.1	<0.1	>99	<0.1	33
	All three	<1	8	54	38	25

^aThis study ^bCousins et al., 2003 ^cRemberger et al., 2005

2.2 Toxicity

The toxicity of phthalates has been described by e.g. Staples et al. (1997), Bradlee and Thomas (2003) and by David and Gans (2003). Bradlee and Thomas reviewed studies on the aquatic toxicity of phthalate esters and concluded that higher phthalate esters (chain length $\geq C6$) do not pose intrinsic toxicity to aquatic organisms. Phthalate esters are rapidly metabolised in biota and their water solubility is low, reducing their bioavailability.

Some evidence exists, which indicates that DEHP and DINP are potential carcinogens (David and Gans, 2003). This evidence mainly consists of observed effects in rats and other laboratory animals at high-level exposure (e.g. Klaunig et al., 2003). Phthalates are non-genotoxic in most test systems and the carcinogenic effect is generally a non-genotoxic mode of action. There are no conclusive evidences for carcinogenic effects in humans (Klaunig et al., 2003; Lapinskas et al., 2005).

Studies have also indicated that DEHP exerts some interference with the endocrine system resulting in “anti-androgen-like” and/or estrogenic effects such as reduced sperm count in males (Andrade et al., 2006; Borch et al., 2006), but the mechanism for this is unclear. Also these effects have mainly been found in rats, and their relevance to humans is strongly questioned by industrial representatives. Another effect called short “ano-genital-distance” (AGD) in male babies has been reported to correlate to concentrations of phthalate metabolites in the mother’s urine during the pregnancy (Swan et al. 2005).

The Swedish Chemicals Agency has identified DEHP as a CMR substance (carcinogenic, mutagenic, reproduction disturbing) and it is a phase-out substance within the prioritisation guide

PRIO (www.kemi.se). None of the other substances included in the current study are listed within PRIO.

2.3 Human exposure and metabolism

Human exposure to phthalates can occur via different routes such as ingestion and uptake via food (or toys for babies and small children), inhalation, and dermal absorption (cosmetics and personal-care products). Once in the body, phthalates are rapidly hydrolysed to their monoesters and these monoesters may in turn be conjugated to their corresponding glucuronides or sulphates (Koch et al. 2003). The conjugated monoesters are excreted in urine and faeces (Albro and Lavenhar, 1989; Calafat et al. 2004; Silva et al. 2004). Thus, when monitoring human exposure to phthalates it is of interest to determine the concentration of the conjugated monoesters rather than the mother compounds.

3 Production, consumption, emissions and regulation

The primary use of phthalates is as plasticisers, and in a global perspective they are the most commonly used plasticisers. In Western Europe, about one million tonnes of phthalates are produced annually (Plasticisers Information Centre, 2007). The primary use of phthalates has been in PVC plastics, but also to a lesser extent in nail polish, perfume, sealants, pigments, adhesives and tool handles. Today, di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), account for the majority of the phthalate use as plasticisers within the EU, and include applications such as wall covering, flooring and medical applications.

In Sweden, a shift in phthalate use occurred between 2000 and 2001, which is mainly connected to a voluntary phase-out of the substance. This is visualised in Figure 1, which shows the Swedish use of DINP, DIDP and DEHP as well as DEHA between 2000 and 2005. As DINP and DIDP are registered under different CAS-numbers, these have been combined and the lines in Figure 1 represent the sum of the two products. The underlying data included in the sum is shown in Figure 2. It is clear from the figures that DEHP has been replaced by DINP, whereas the consumption of DIDP has remained fairly constant over the last five years. The number of applications for phthalate use, which is linked to the total consumption, has decreased by approximately 50 % for DEHP containing product categories, whereas the number of applications for DINP has increased by more than 80 % (SPIN, 2007).

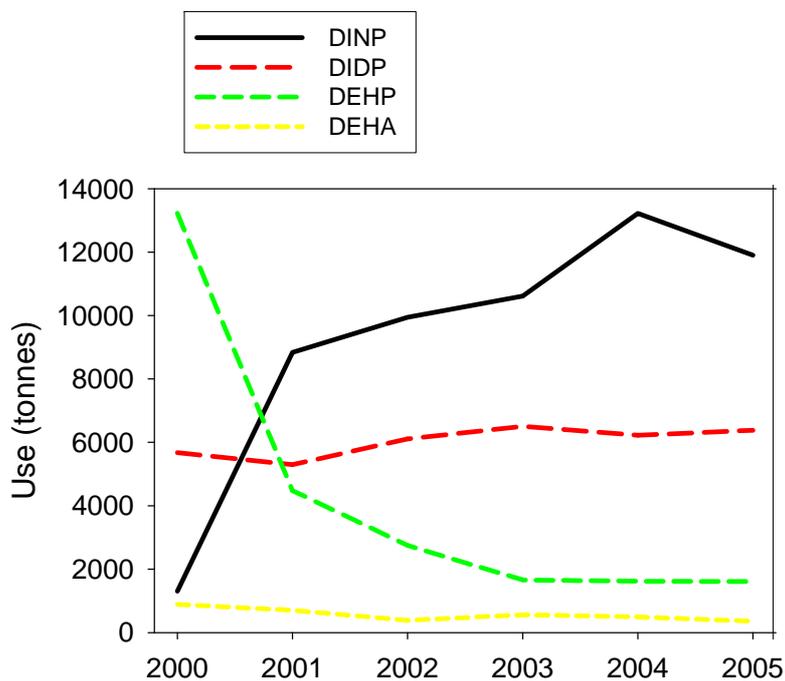


Figure 1. The Swedish use of phthalates and DEHA between the years 2000 and 2005 (SPIN, 2007).

In 2004, 56 tonnes of DINP and 350 tonnes of DIDP was produced in Sweden, which can be compared with the total import of 18 300 tonnes. The production of DEHP was not reported but the import was just under 600 tonnes in 2004 (KEMI and SCB, 2006).

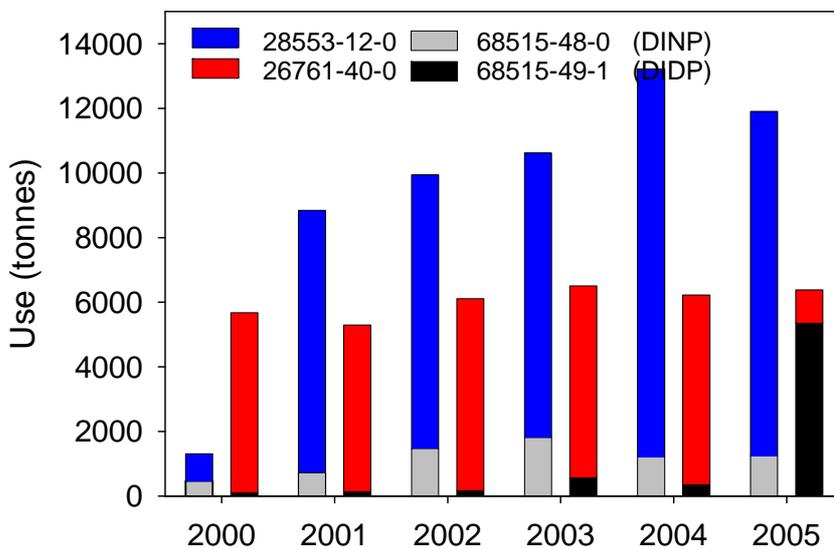


Figure 2. The Swedish use of DINP and DIDP and the distribution between the different CAS-numbers (SPIN, 2007).

In addition to the substances presented above, four additional phthalates were analysed in air. These were di-ethyl phthalate (DEP), di-*iso*-butylphthalate (DIBP), di-n-butylphthalate (DBP) and butylbenzyl phthalate (BBzP). These substances were used in amounts and products according to Table 5. The figures concern the year 2005.

Table 5. Swedish use of four additional phthalates in 2005 (SPIN, 2007)

Substance	Main use	Total use (tonnes)
DEP	61 preparations, mainly solvents	15
DIBP	102 preparations, mainly glues, fillers, process regulators	49
DBP	144 preparations; mainly glues, paints, fillers, process regulators, colouring agents, surface treatment	210
BBzP	119 preparations; mainly softeners, construction materials, fillers and paints	727

3.1 Emissions

The Swedish consortium SMED (Swedish Methodology for Environmental Data; www.smed.se), is a collaborative consortium involving four organisations with the main task is to gather and develop Swedish competence within emission statistics related to the national abatement efforts within the areas emissions to air and water, waste/waste management, and hazardous substances/toxic chemicals.

The emissions of DEHP in Sweden have previously been estimated within SMED (Palm et al., 2005; Brorström-Lundén et al., 2004; Carlsson et al., 2004). The estimated DEHP emissions were 143 - 432 tonnes to air per year in 2001/2002 and about 178 tonnes per year to water. Of these estimates, the majority was expected to be a result of diffuse emissions from products in use. To our knowledge, no Swedish emission inventories have been performed for DINP or DIDP.

3.2 National and EU legislation on phthalates

A new EU directive (2005/84/EC) came into force on January 16, 2007. This directive has been implemented in the national legislation act KIFS 1998:8, chapter 10, §4b. It concerns the phthalates DEHP, DBP (dibutyl phthalate), BBzP (butylbenzyl phthalate), DINP, DIDP and DNOP (di-n-octyl phthalate) and implies that the three previous compounds may not be used in concentrations (sum of three) above 0.1 % per mass in toys and childcare products. The three latter may not be used in concentrations (sum of three) above 0.1 % per mass in toys and childcare products that children may put in their mouth. The new legislation modifies the previous rules by specifying six phthalates of concern as well as a concentration limit. It also removes the age limit for toys and concerns all children's products. Finally it removes the formulation "can be placed in the mouth by children" for the three phthalates DEHP, DBP and BBzP.

In addition to this directive, the risk assessment for DEHP (ECB, 2001), which was undertaken by the Swedish Chemicals Agency, KEMI, generated an agreement within the expert group that DEHP should be banned for use in products intended for outdoor use and in plastic treating facilities with poor emission control. It is possible that such restrictions will be discussed within the framework for the new EU legislation for chemicals, REACH.

4 Previous measurements in the environment

Monitoring data on iso-phthalates are scarce, which also has been stated in the EU risk assessments (ECB, 2003a,b). The few monitoring data available have been compiled in the risk assessments and are summarised in Table 6. Numerous studies have been performed in the past considering the environmental levels of DEHP, which are available in the full risk assessment report (ECB, 2001). For the purpose of this study, we have focussed on obtaining previous data for *iso*-phthalates as these were the main target compounds in the current screening.

Table 6. Measured concentrations of iso-phthalates in various matrices in the environment (Source: ECB, 2003a,b and references therein).

Matrix	DINP	DIDP
Sewage sludge [µg/kg dw]	4 - 23 000 4 760 - 13 800	3 800- 8 030
Sediment [µg/kg dw]	<100 - 250 <25 - 6 161	<100 - 190 <15 - 1 109 (median: <15)
Biota [µg/kg dw]	<500 - 810 (mussels)	<200 - 1 240 (mussels)

5 Sampling strategy and study sites

5.1 National

A national sampling strategy was developed in order to determine the concentrations of phthalates in different environmental matrices in Sweden. An additional aim of the sampling was to identify major emission sources as well as important transport pathways. The sampling programme was therefore based on identified possible emission sources and use of the chemicals as well as on the behaviour of the substances in the environment. The programme included both measurements in background areas and close to potential point sources. Measurements of various samples from urban areas in conjunction with sludge samples from municipal waste water treatment plants were used to identify emission from the society. Food-stuffs and human urine samples were analysed in order to investigate the potential for human uptake. The sampling programme is summarised in Table 7.

Table 7. National sampling programme

Site	Air	Sediment	Sludge	Fish	Food-stuffs	Urine	Total
Background							
Råö	3						3
Gårdsjön				3			3
National background lakes		3		3			6
Point source							
Stenungsund (various industries)	3	6		3			12
Gislaved (plastic and rubber plant)	3						3
Diffuse sources							
National municipal STPs			6				6
Stockholm	3	3					6
Human exposure							
Various					6	6	12
Total	12	12	6	9	6	6	51

Two industrial sites were selected as possible point sources for phthalates; one with plastics and former rubber production (Gislaved) and one with various industries such as chemical and plastics production (Stenungsund).

As diffuse sources, six wastewater treatment plants were selected, which are all included in the Swedish Environmental Protection Agency's monitoring programme for environmental pollutants in sludge (Naturvårdsverkets miljöövervakningsprogram av miljögifter i slam). Diffusive pathways were also studied in an urban area in Stockholm, where air and sediment samples were collected.

In order to determine background levels; air, sediment and biota samples were collected.

Air samples were collected at Råö which also is a station in the national monitoring programme for air pollutants and in the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) network.

From three national background lakes sediment and fish were collected. The lakes are used within the national monitoring programme of contaminants in biota. The samples were delivered by the Swedish Museum of Natural History.

5.2 Regional

A regional screening programme was carried out by different Swedish county administrative boards that had the possibility to collect and send samples to IVL for analysis. In the case of phthalates, three county administrative boards participated in the regional sampling programme with a total of 11 samples consisting 10 sludge samples and one sediment sample. The details of the samples are shown in the Appendix.

6 Methods

6.1 Sampling

Air samples were collected using a low volume air sampler (LVS) with a flow of approximately 1 m³/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 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 methyl-*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 collected **sludge** samples from the anaerobic chambers. The sludge was transferred into plastic jars (phthalate free polypropylene) and stored in a freezer (-18°C) until analysed.

Surface **sediment** (0-2 cm) samples were collected by means of a Kajak sampler. The sediment was transferred into pre-heated (400°C) glass jars and stored in a freezer (-18°C) until analysed. Glass jars were preferred to plastic considering the expected low concentrations in sediments. Three sediment samples from the national background lakes were provided from the specimen bank at The Swedish Museum of Natural History. These samples were stored at -18°C in pre-cleaned glass jars.

The **fish** samples were collected by means of fishing net or hoop net. The fish samples were individually wrapped in cleaned aluminium foil and stored in freezer (-18°C) until analysed. Fish muscle was dissected for analysis by means of solvent washed scalpels. Samples of dissected fish muscle from three national background lakes were provided from the specimen bank at The Swedish Museum of Natural History. These samples were stored at -18°C in pre-cleaned glass jars.

The **food-stuffs**, mixture of vegetables, mixed dairy products; homogenised fish and cooking fat were provided by the National food administration.

The **urine** samples were provided by the University Hospital of Lund (Department of Occupational and Environmental Medicine (Staffan Skerfving). The samples were collected from women (age 34-51) in connection to mammography.

6.2 Analysis

6.2.1 General remarks

Phthalates are recognised as ubiquitous pollutants in indoor as well outdoor environments (Furtmann, 1995). Therefore, it is not surprising that phthalates are generally detected even in fine chemicals ultra pure water, organic solvents used for extraction and laboratory equipment (Tienpont et al., 2005). Special routines are therefore essential in order to guarantee the integrity of

the samples. The routines used at the laboratory in order to minimise the risk for contamination of the samples are briefly described below.

All glass equipment were wrapped in aluminium foil and heated to 400°C for 4 hours. The aluminium foil prevents re-contamination of the equipment until used. All equipment made of Teflon and metal was washed with solvent before use.

In order to avoid contamination from the laboratory air during Soxhlet extraction of the air samples, the outlet of the cooler was protected from ambient (contaminated) air by an activated charcoal column. In this manner the Soxhlet was working as a closed system. This is important since indoor air concentrations generally are quite high (Tienpont et al., 2005).

During the whole analytical procedure samples, extracts, solvents and chemicals were carefully protected from air precipitation and dust that proved to be a source of phthalates. This was accomplished by the covering of test tubs, jars and other equipment with clean aluminium foil (Parkman & Remberger, 1995).

All solvents used were of the highest quality available and were checked before used. Ultra pure water was produced by Milli-Q equipment. Batches of water from this equipment were stored in glass containers and were checked prior to use. The checked batches of solvents and water were exclusively applied for this project. Chemicals and equipment such as Na₂SO₄, aluminium foils, aluminium oxide (ALOX), silicon gel were thermally treated at 400°C before used.

Certified reference standard was used to quantify the single compound phthalates (e.g. diethyl-, dibutyl-, di-(2ethylhexyl) phthalate). DINP and DIDP are complex mixtures of isomers and appear in gas chromatograms (Figure 3) as partly unresolved “humps” in a quite broad retention window (about 4 min). Different production routes (see 2.1) of the isomeric alcohol mixtures used for the manufacture of DINP and DIDP results in different branching. However, it was not possible to distinguish DINP or DIDP originating from different production routes. Standards recommended by ECPI (European Council for Plasticizers & Intermediates, a sector group of CEFIC, March 26, 2000) were used. Isotopically labelled DEHP (D₄-DEHP) was used as recovery standard.

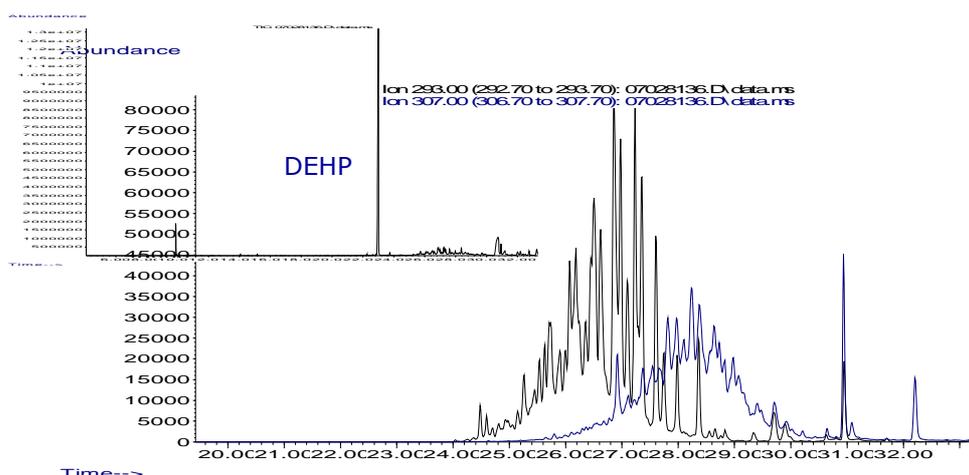


Figure 3. Chromatograms of the iso-phthalates DINP and DIDP and the single substance phthalate DEHP (small picture). Equal amounts give approximately equal areas under the curve hence iso-phthalates are more difficult to distinguish from background noise.

6.2.2 Air, sludge and sediment

Filters and PUF-columns used in the **air** sampling were spiked with recovery standard (D₄-DEHP) and extracted with pentane:MTBE in a Soxhlet apparatus for 6 hours. The concentrated extract (blown down with clean N₂) was cleaned-up on a silica gel column prior GC-MS analysis.

The pore water in the **sediment** and **sludge** samples was separated by centrifugation before the extraction. The sample was fortified with recovery (D₄-DEHP), mixed carefully and subsequently extracted with (a) acetone, (b) acetone and MTBE and (c) acetone and pentane:MTBE (3+1). The acetone in the pooled extract was washed away by extraction with ultra pure water. The organic extract was safeguarded after phase separation. The water phase was extracted one more time with a mixture of pentane and MTBE. The combined extract was subjected to clean-up on a silica gel column and subsequently on an amino propylene column prior to GC-MS analysis.

6.2.3 Fish, food-stuffs and human urine samples

Fish samples (muscle, 10 g) were spiked with recovery standard (D₄-DEHP) and homogenised in acetonitrile. The extract was safeguarded and the samples were extracted once more with acetonitrile. The extracts were combined and the acetonitrile removed by shaking with water and pentane. The extracts were dried, concentrated and the solvent changed to hexane followed by clean-up on an ALOX column prior to GC-MS analysis.

The **food-stuff** samples were essentially treated in the same way as the fish samples with the exception of cooking fat, which was extracted with pentane:MTBE and the lipids in the extract was separated by means of gel permeation chromatography. Finally, a short ALOX column was used to polish the extract prior to analysis on GC-MS.

The **urine** samples were analysed for the conjugated monoesters produced in the human metabolism of phthalates. These conjugated monoesters are very water soluble and must be de-conjugated prior to extraction. The method used was based on the methodology described by Blount et al. (2000), Koch et al. (2003) and Silva et al. (2004). Briefly, urine samples were buffered with ammonium acetate and mixed with labelled recovery standard (¹³C₄-MEHP) and β-glucuronidase enzyme without any lipase activity (β-glucuronidase; *E. coli* K 12; Blount et al., 2000). The samples were incubated at 37°C over night. After hydrolysis, the samples were acidified and concentrated by means of SPE-columns. The extracts were derivatised with diazomethane and cleaned up on a silica gel column.

6.2.4 Instrumentation

The phthalate extracts were analysed on a 6890N gas chromatograph connected to a 5973N mass selective detector (Agilent). The injection, 1 µl, was done in splitless mode at 240°C. The fused silica capillary column (VF-5MS 30 m × 0.25 mm i.d. × 0.25 µm film thickness, Varian) was held at 45°C for 1 min., ramped 15°C/min to 200°C, 5°C/min until 300°C and held at 300°C for 2 min. Helium was used as carrier gas. The detector was used in selected ion monitoring mode (SIM) with electron ionisation at the energy 70 eV. The analytes were identified by their characteristic retention time and one target ion used for quantification. One or two qualifier ions (Q-ion) was used to increase specificity (Table 8) Quantification was based on comparison of peak abundance to the known response of the internal standard (D₄-DEHP). The reported analyte concentrations were corrected according to the determined surrogate standard losses.

Table 8. Target ion (Tgt-ion) and qualifier ion (Q-ion) utilised in the MS-quantification

Compound	Tgt-ion	Q-ion 1	Q-ion 2	Mw
DEHA	129	149	241	370
DEHP	149	167	-	390
DINP	293	294	-	418
DIDP	307	308	-	446
D ₄ -DEHP	153	171	-	394
¹³ C ₄ -MEHP	167	153	-	296
MEHP	163	149	-	292
MINP	163	149	-	306
MIDP	163	149	-	320

Abbreviations: di-(2-ethylhexyl)-adipate (DEHA); di-(2-ethylhexyl)-phthalate (DEHP); di-iso-nonylphthalate (DINP); di-iso-decylphthalate (DIDP), mono-(2-ethylhexyl)-phthalate (MEHP); mono-iso-nonylphthalate (MINP); mono-iso-decylphthalate (MIDP)

7 Results and discussion

7.1 Air

The results from the measurements of phthalates in air are presented in Figure 4, Figure 6 and in the Appendix.

Phthalates were found in all air samples (Figure 4). DINP and DIDP were detected in 83 and 67 % of the samples respectively in concentrations of 0.3-1.1 ng/m³ and 0.3-5.5 ng/m³ respectively. DIDP was not detected in background air samples (<0.3 ng/m³) and DINP only in one. The most abundant substance in the atmosphere was DEHP with concentrations of 0.5 – 1.1 ng/m³ in air from background sites and up to 3 ng/m³ in air from the point source in Gislaved. Present results are in the same concentration range as reported by Thurén et al. (1991) but Thurén also detected significantly higher levels of DEHP in some urban air samples (up to 77 ng/m³). Thurén observed a negative correlation of DEHP concentrations to air temperature (season) which not is obvious in the data from this study. The corresponding adipate, DEHA was also found in all samples but one, but in lower concentrations (factor of 2-20 lower than DEHP).

DEHP generally occurred in higher concentrations than the *iso*-phthalates (Figure 5), with the exception of three samples (urban air – see Figure 4), where DIDP dominated. This pattern does not agree with the current consumption pattern in Sweden, suggesting that the total use of DEHP now is 3-6 times lower than the use of DINP and DIDP (Figure 1). However, because of its higher volatility, larger amounts of DEHP may be expected to reach the atmosphere. The observed pattern may also be a result of DEHP still being contained in various products in the technosphere giving rise to diffuse emissions resulting in the higher atmospheric levels. It is likely that over time, the observed atmospheric levels of DEHP will decrease, whereas possibly the concentrations of other phthalates will increase.

Remarkable is the high concentration of DIDP found in Stockholm relative to the other phthalates, considering that the use of DIDP corresponds to about 50 % of the use of DINP. The level of DIDP in urban air seems to increase over the sampling period December to March. Also in Stenungsund and Gislaved elevated concentrations of DIDP were found in air on one occasion. It is unclear what causes these elevated levels.

The adipate, DEHA, occurred in lower concentrations compared with the phthalates, which was expected considering the lower consumption level of this substance (Figure 1).

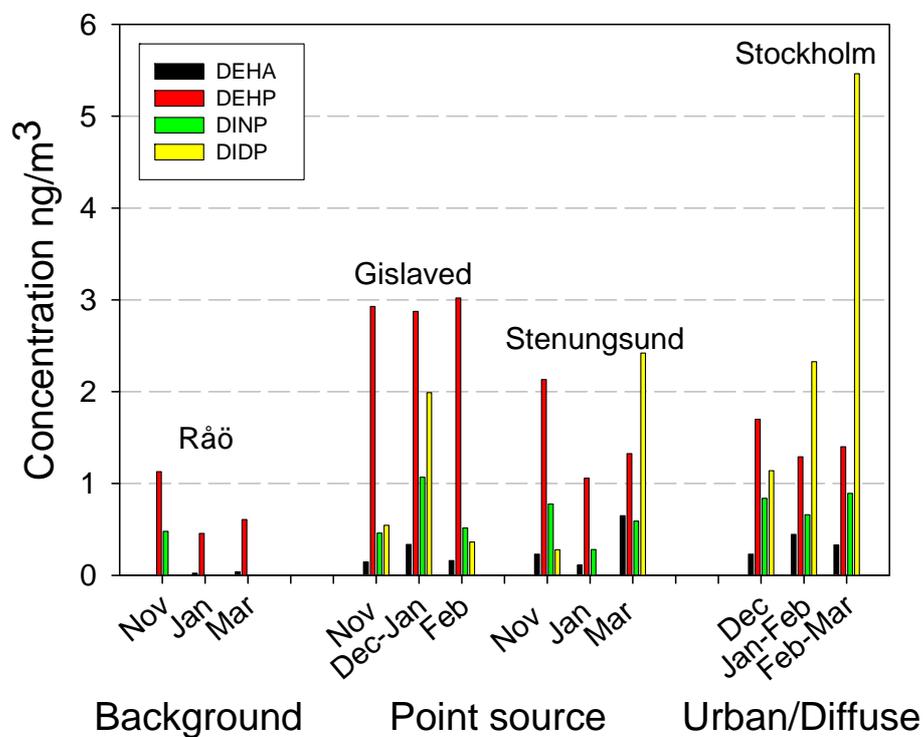


Figure 4. Concentrations of DEHA, DEHP, DINP and DIDP in atmospheric samples.

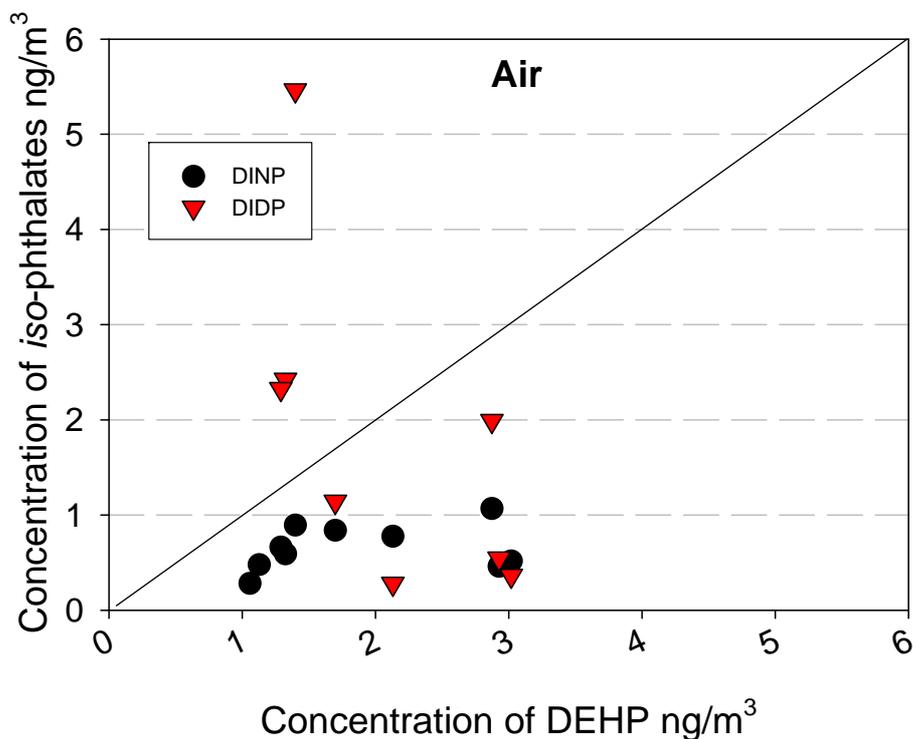


Figure 5. Concentration of iso-phthalates as compared to the concentration of DEHP in air samples

Figure 6 shows the results from the measurements in air of the four additional phthalates. The relationship between the four (DEP, DIBP, DBP, BBzP) varies from 3:14:8:1 in background air, 3:16:350:1 in Gislaved, 3.5:24:9:1 in Stenungsund to 8:10:20:1 in urban air. In particular the relative amount of DBP compared to the other three substances varies greatly from site to site, with lowest abundance in background air, and highest occurrence outside Gislaved. The DBP levels in Gislaved were actually up to 5 times higher than the measured levels of DEHP, despite the lower national consumption of this substance, indicating that there might be a source in that particular area. Also in the urban area, the levels of DBP were elevated compared to background air. In the urban area, levels of DEP were about 10 times higher compared to the other sites. This substance is mainly used in solvents of different kinds. BBzP was the phthalate showing the lowest concentrations in air.

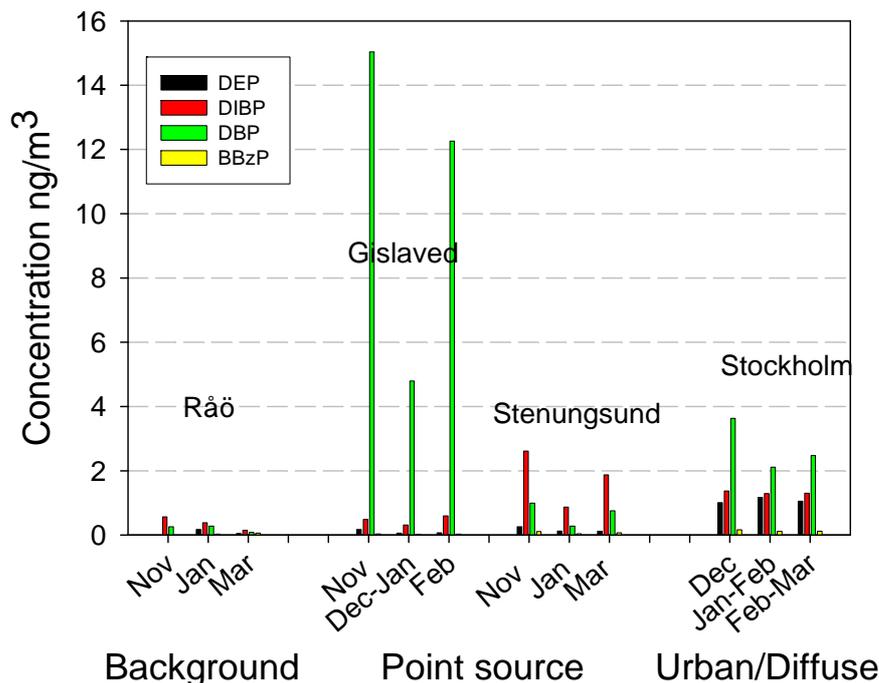


Figure 6. Concentration in air of four additional phthalates: DEP, DIBP, DBP, BBzP.

7.2 Sediments

Sediment samples can give useful insights to the historical burden of chemical contaminants. In the current study, solely surface sediments (0-2 cm) have been analysed, roughly representing the last 2-5 years, depending on local sedimentation rates. This means that the sediments can be expected to reflect the emission situation a number of years ago, whereas the current release pattern may be expected to show in a few years time.

Figure 7 shows the results of the measurements in sediments. Phthalates and DEHA were not detected in background sediments (detection limit DINP: 100, DIDP:100, DEHA: 30 µg/kg dw, DEHP: 40 µg/kg dw). However, they did occur in sediments outside the industrial site in Stenungsund, but the levels were low compared to the concentrations found in the sediment samples collected in Stockholm. This supports the theory that diffuse emissions are the most important. The levels of DEHP found in urban sediments (1200-2800 µg/kg dw) were of similar order of magnitude as those previously measured by Sternbeck et al. (2003) which varied between 510 and 2300 µg/kg dw at the same sites. Interestingly, the levels of DEHP are of the same order of magnitude as DINP and DIDP, which roughly corresponds to the usage pattern in 2001 (see Figure 1). This indicates that the surface sediments mirror the consumption pattern approximately five years ago. The fact that DEHP levels in sediments have not decreased despite decreased usage further reflects this “time lag”. The levels of DINP and DIDP found in urban sediments were similar to or slightly higher than reported levels in the EU risk assessment (DINP: <100 - 3200 compared to <25 - 6161 µg/kg dw; DIDP: <100 - 3400 compared to <15-1109 µg/kg dw). This may be a result of continued or increased use, or simply a reflection of geographical variation. In addition to the national sampling programme, one regional sediment sample representing the landfill site Strandmossen in Kristinehamn was analysed. All the phthalates were found in this

sample, but in relatively low levels compared to the urban sediments; DINP: 440 µg/kg dw, DIDP: 290 µg/kg dw, DEHP: 400 µg/kg dw.

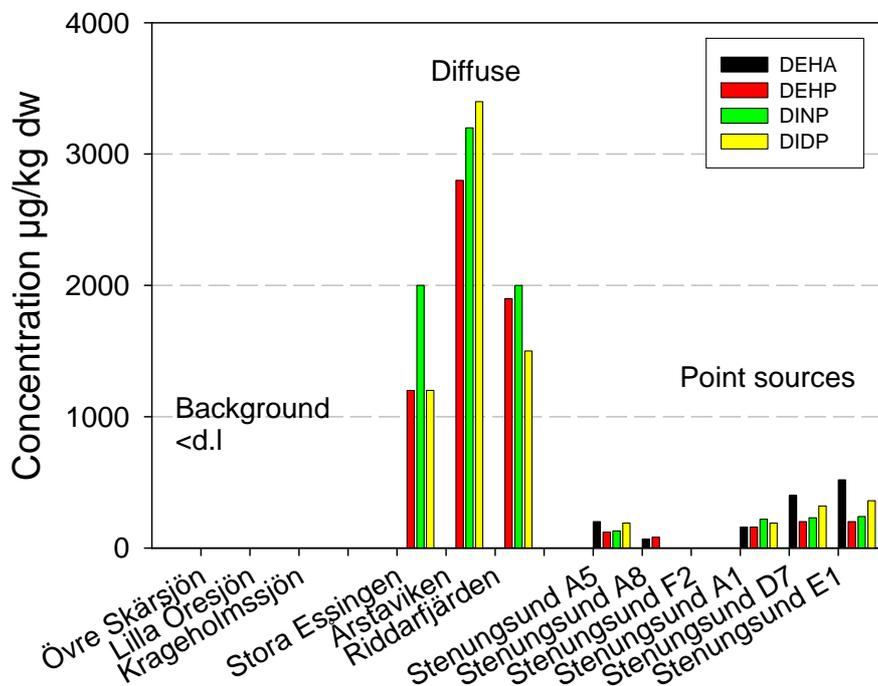


Figure 7. Concentration of phthalate esters and DEHA in sediments

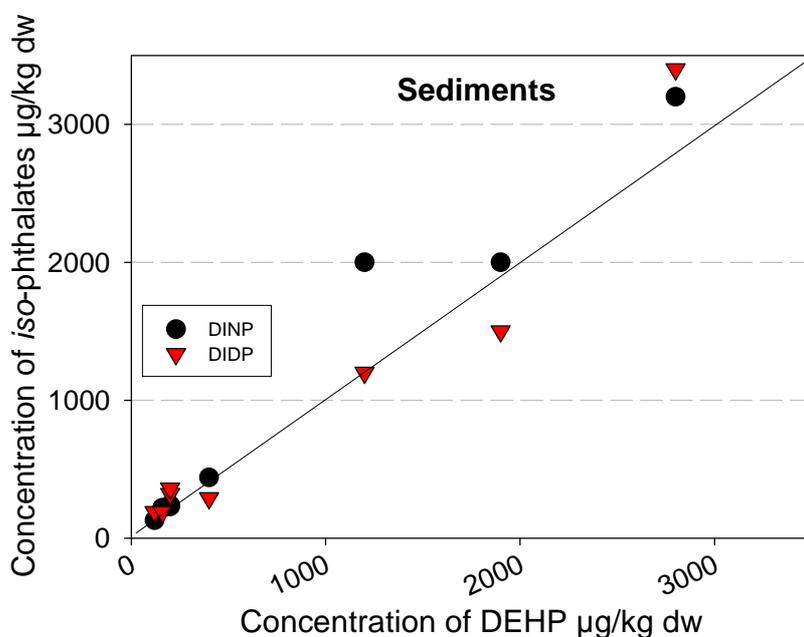


Figure 8. Concentration of iso-phthalates as compared to the concentration of DEHP in sediment samples.

7.3 Biota

DINP and DIDP were not found in any of the fish samples. DEHP was detected in 4 out of 12 samples in levels ranging from 15 – 26 µg/kg fresh weight. DEHA was only detected in two samples.

7.4 Sludge

Figure 9 shows the measured concentrations of phthalates in sludge. The concentrations found in the samples collected in the national and regional programmes have been combined in the figure. All the phthalates included were found in all of the sludge samples and no large variation between the different sewage treatment plants was observed. DEHP has been measured in a previous screening study concerning the plasticizer adipates (Remberger et al. 2005). The concentrations found in that investigation were generally somewhat lower than in the present investigation. This is unexpected, considering the substitution of DEHP with DINP and DIDP.

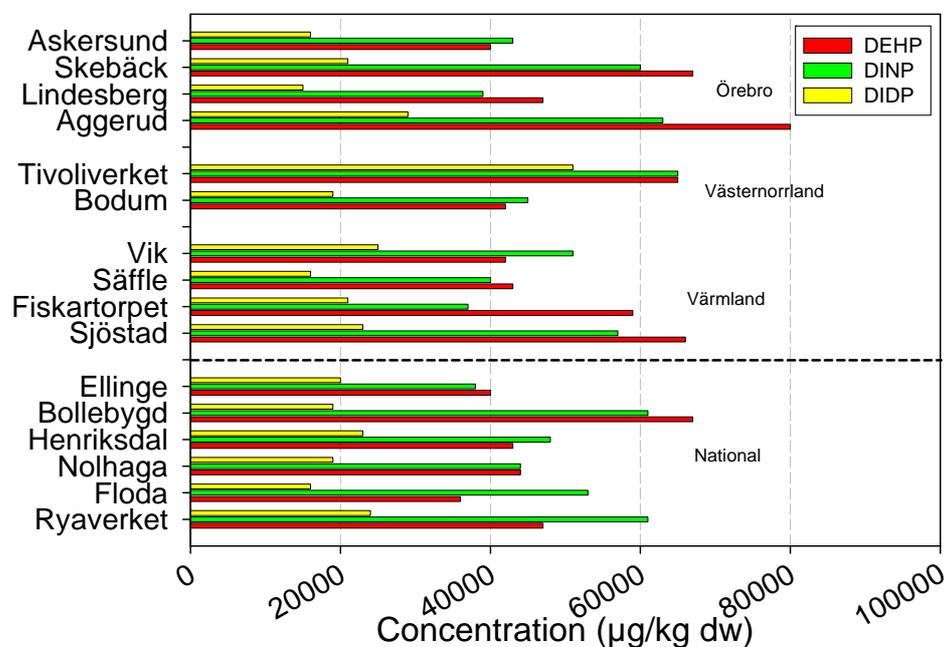


Figure 9. Concentration of phthalate esters and DEHA in sludge from municipal sewage treatment plants.

DINP occurred in concentrations which were in the same order of magnitude as DEHP, whereas DIDP concentrations were around 50 % of the DEHP levels (Figure 10). As in the case of air, the observed pattern does not quite match the current consumption pattern in Sweden as DINP and DIDP are the most commonly used substances today. The large volumes of DEHP stored in the technosphere may explain the high abundance in sewage sludge. The fact that the DINP/DEHP ratio is closer to the current consumption pattern in sludge samples than in air samples may partly be explained by the fact that DINP due to its lower volatility and higher logKow-value is more likely to be found in sludge than in air.

DEHA was only found in the sludge samples from Ellinge (110 µg/kg dw) and Askersund (180 µg/kg dw).

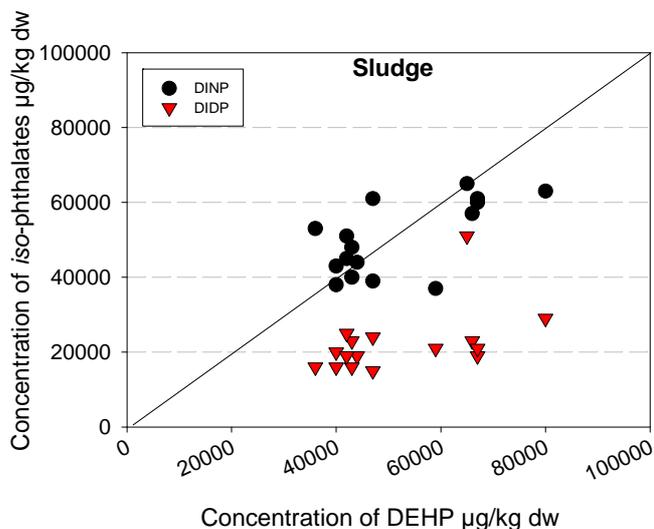


Figure 10. Concentration of iso-phthalates as compared to the concentration of DEHP in sludge.

The levels of iso-phthalates in sludge (DINP: 37000-65000 µg/kg dw; DIDP; 15000-51000 µg/kg dw) are higher than reported levels in the EU risk assessment (DINP: 4-23000 µg/kg dw; DIDP 3800-8030 µg/kg dw; ECB 2003 a, b).

7.5 Foodstuffs

Figure 11 shows the results from the measurements of phthalates in foodstuffs. DINP was detected in two out of six samples: in one vegetable sample and in the cooking fat sample. DIDP was only detected in one sample of vegetables. The most frequently detected substance was DEHP, which was found in all samples analysed, in one sample of vegetables the concentration was as high as 1900 µg/kg fw. Also DEHA was found in all samples but in lower levels. It is evident from Figure 11 that the current levels of *iso*-phthalates still are fairly low compared to levels of DEHP. Thus, these measurements indicate that the human exposure to *iso*-phthalates via ingestion of food at present is reasonably low compared to the exposure to DEHP.

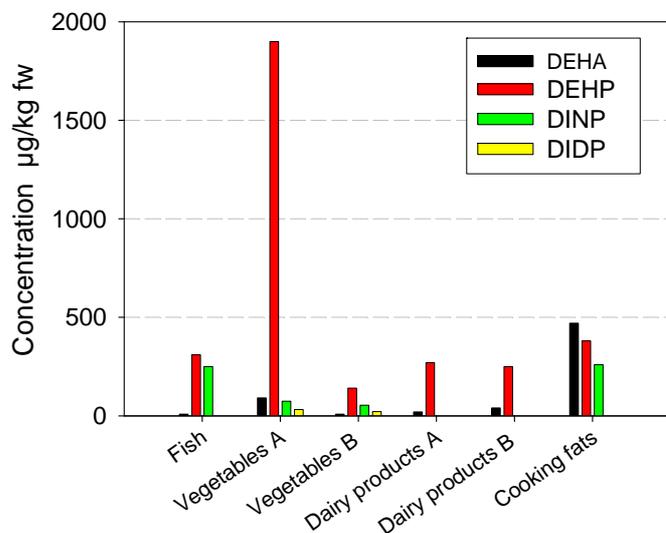


Figure 11. Concentration of phthalates and DEHA in various foodstuffs.

7.6 Urine

Metabolites of DEHP and iso-phthalates were found in all the analysed samples of human urine in concentrations of 0.7-11 µg/L for MEHP (monoethylhexylphthalate, metabolite of DEHP). Monoesters of DINP and DIDP could not positively be detected (<50 µg/l). As the detection limit was at least 5 times as high as the detected concentrations of MEHP, the human exposure to these phthalates could not be compared to DEHP-results. The measured concentrations of MEHP are in agreement with previous reports (Koch, et al., 2003).

The various routes of human exposure to phthalates are numerous, and include sources such as intake of food, inhalation of indoor (and outdoor) air and use of personal care and cosmetic products. It occurs from Figure 11 that the exposure to *iso*-phthalates via food should be low compared to the exposure to DEHP, but then, as described above there are other routes of exposure, which have not been investigated in this study. Due to the differences in detection limits, it is not possible to judge whether the human exposure to *iso*-phthalates is comparable to the exposure to DEHP.

8 Conclusions

The following conclusions can be drawn from the screening study:

- *Iso*-phthalates were detected in air, sediments, sewage sludge and foodstuffs.
- There are on-going emissions of *iso*-phthalates to the Swedish environment.
- Concentrations in air in background areas were generally low, thus long-range atmospheric transport does not seem to be of major importance.
- In air, the levels of *iso*-phthalates are still generally lower than DEHP levels, with the exception of urban air, where DIDP dominates. We recommend further measurements of *iso*-phthalates in urban air, ventilation outlets from buildings to explore the contribution from the indoor environment and possibly also air near industrial facilities, in order to investigate the high levels of DIDP.
- In sediments and sludge the DINP levels are of similar order of magnitude as the levels of DEHP. In sediments this is true also for DIDP, whereas DIDP levels in sludge correspond to about 50 % of the DEHP levels.
- Uptake of phthalates in biota seems to be limited.
- Human exposure to *iso*-phthalates cannot be assessed in comparison to the exposure to DEHP. Metabolites of *iso*-phthalates were not found in human urine but detection limits were approximately five times higher than detected levels of metabolites of DEHP. The levels in food-stuffs are still higher for DEHP than for *iso*-phthalates. Additional routes of exposure should also be investigated, e.g. inhalation of indoor air.
- The current pattern of environmental levels seems to mirror the consumption pattern five years ago – thus reflecting a time lag which may be explained by the large amounts of DEHP still present in the technosphere despite a decrease in use.
- As there are no set risk levels of *iso*-phthalates, and due to ambiguous data on toxicity it is not possible to determine the risk of their presence in the environment.

9 Acknowledgements

Thanks to the staff at the regional municipalities that have contributed to the sampling. Especially thanks to Anders Bignert, NRM for contributing with samples for the national programme and to The Environment and Health Administration in Stockholm for letting us use their sampling station for air. We also want to thank Staffan Skerfving at the University Hospital of Lund (Department of Occupational and Environmental Medicine) for providing the urine samples. The study was funded by Environmental Monitoring at the Swedish Environmental Protection Agency.

10 References

- Albro, P. W. and S. R. Lavenhar (1989). "Metabolism of di(2-ethylhexyl)phthalate." *Drug metabolism reviews* 21(1): 13-34.
- Andrade, A. J., Grande, S. W., Talsness, C. E., Grote, K., Golombiewski, A., Sterner-Kock, A., et al. (2006). A dose-response study following in utero and lactational exposure to di-(2-ethylhexyl) phthalate (DEHP): effects on androgenic status, developmental landmarks and testicular histology in male offspring rats. *Toxicology* 225(1):64-74.
- Blount, C. B., Milgram, E. K. Silva, J. M. Malek, A. N. Reidy, A. J. Needham, L. L. and Brock, J., (2000). Quantitative Detection of Eight Phthalate Metabolites in Human Urine Using HPLC-APCI-MS/MS. *Anal. Chem.* 72(17): 4127-4134.
- Borch, J, Axelstad, M., Vinggaard, A. M, Dalgaard, M., (2006). Diisobutyl phthalate has comparable anti-androgenic effects to di-n-butyl phthalate in fetal rat testis. *Toxicol Lett* 163(3):183-190.
- Bradlee C.A, Thomas P. (2003). Aquatic Toxicity of Phthalate Esters. In: *The Handbook of Environmental Chemistry. Volume on Phthalate Esters.* Editor: C.A. Staples. Springer-Verlag, Germany.
- Brorström-Lundén E., Andersson J., Palm A., Segersson D., Isaksson L., Brånvall G. (2004). Utsläpp åren 2001 och 2002 av farliga ämnen för rapportering enligt vattendirektivet. SMED rapport. *In Swedish*
- Calafat, M. A., R. A. Slakman, Silva, J. M., Herbert, R. A., Needham, L. K (2004). "Automated solid phase extraction and quantitative analysis of human milk for 13 phthalate metabolites." *J. Chromatogr. B* 805: 49-56.
- Carlsson A., Sternbeck J., Looström-Urban H., Skårman T., Villner M., Sjödin Å. (2004). Modellerings av emissioner från icke-rapporterande punktkällor – exemplet xylen och DEHP. SMED rapport. *In Swedish*
- Cousins I.T., Mackay D. Parkerton T.F. (2003). Physical-Chemical Properties and Evaluative Fate Modelling of Phthalate Esters. In: *The Handbook of Environmental Chemistry. Volume on Phthalate Esters.* Editor: C.A. Staples. Springer-Verlag, Germany.
- David R., M., Gans G. (2003). Summary of Mammalian Toxicology and Health Effects of Phthalate Esters. In: *The Handbook of Environmental Chemistry. Volume on Phthalate Esters.* Editor: C.A. Staples. Springer-Verlag, Germany.
- ECB. 2001. Risk Assessment of bis(2-ethylhexyl) phthalate. R042_0109_env_hh_0-6
- ECB. 2003a. Risk assessment of 1,2-benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate (DINP) Series: 2nd Priority List Volume: 35
- ECB. 2003b. Risk assessment of 1,2-Benzenedicarboxylic Acid, di-C9-11-Branched Alkyl Esters, C10-Rich And Di-"Isodecyl" Phthalate (DIDP) Series: 2nd Priority List Volume: 36
- Furtmann, K. (1995). "Phthalate analysis as a tool for environmental assessment." *Analytical methods and Instrumentation* 2(5): 254-265.
- KEMI and SCB. 2006. MI 45 SM 0601. Miljö- och hälsofarliga kemikalier 2004. *In Swedish*

- Klaunig, J. E., Babich, M. A., Baetcke, K. P., Cook, J. C., Corton, J. C., David, R. M., et al. 2003. PPARalpha agonist-induced rodent tumors: modes of action and human relevance. *Crit Rev Toxicol* 33(6):655-780.
- Koch, H. M., Rossbach, B., Drexler, H., and Angerer, JK., (2003). Internal exposure of general population to DEHP and other phthalates - determination of secondary and primary phthalate monoester metabolites in urine. *Environ. Res.* 93: 177-185.
- Lapinskas, P. J., Brown, S., Leesnitzer, L. M., Blanchard, S., Swanson, C., Cattley, R. C., et al. 2005. Role of PPARalpha in mediating the effects of phthalates and metabolites in the liver. *Toxicology* 207(1):149-163.
- Koch, H. M., B. Rossbach, Drexler, H., Angerer, J. (2003). "Internal exposure of general population to DEHP and other phthalates - determination of secondary and primary phthalate monoester metabolites in urine." *Environ. Res.* 93: 177-185.
- Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E. 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* Vol. 15 pp 1627-1637.
- Palm A., Jeanette Andersson, Eva Brorström-Lundén. 2005. Översiktlig kartläggning av farliga ämnens huvudsakliga spridningsvägar i Sverige. 1. Diffusa källor. SMED rapport. *In Swedish*
- Plasticisers Information Centre. 2007. Website created by ECPI, the European Council for Plasticisers and Intermediates. <http://www.plasticisers.org>.
- Parkman, H., Remberger, M., 1995, "Phthalates in Swedish sediments". IVL B 1167.
- Remberger M., Andersson J., Palm Cousins A., Kaj L., Ekheden Y., Dusan B., Brorström-Lundén E., Cato I. 2005. Results from the Swedish National Screening programme 2004. Subreport 1: Adipates. IVL Report B1645.
- Sharpe RM. 2005. Phthalate exposure during pregnancy and lower anogenital index in boys: wider implications for the general population? *Environ Health Perspect* 113(8):A504-505.
- Silva, J. M., R. A. Slakman, A. J. Reidy, L. J. Pteau Jr, R. A. Herbert, E. Samander, L. L. Needham and M. A. Calafat (2004). "Analysis of human urine for fifteen phthalate metabolites using automated solid-phase extraction." *J.Chromatogr. B.* 805: 161-167.
- SPIN. 2007. Substances in Products in Nordic Countries. <http://195.215.251.229/DotNetNuke/default.aspx>, August, 2007
- Staples, C. A., Adams W. J., Parkerton, T. F., Gorsuch, J. W., Biddinger, G. R., Reinert, K. H. (1997). Aquatic Toxicity of Eighteen Phthalate Esters. *Environ. Toxicol. Chem* 15:875-981.
- Swan S. H., Main K. M., Liu F, Stewart S. L., Kruse R. L., Calafat A. M., et al. 2005. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ Health Perspect* 113(8):1056-1061.
- Tienpont, B., F. David, E. Dewulf and P. Sandra (2005). "Pitfalls and solutions for the trace determination of phthalates in water samples." *Chromatographia* 61(7-8): 365-370.
- Thurén, A. and Larsson, P., 1990, Phthalates esters in the Swedish atmosphere. *Environ. Sci. Technol.*, 24, 554-559.:

Appendix Information on samples and lists of results

Table A 1. List of samples for phthalate analysis, national sampling programme.

Category	Sample ID	Site	Matrix	Notes	Sampling date	X(RT90)	Y(RT90)
Background		Råö-1	air		06-11-01 - 11-30		
Background		Råö-2	air		07-01-02 - 01-29		
Background		Råö-3	air		07-03-05 - 04-02		
Background	5375	Gårdsjön	fish	perch			
Background	5376	Gårdsjön	fish	pike			
Background	5654	Gårdsjön	fisk	perch	2007-04-25		
Background	4687	Tärnan	fish	Perch Swedish Museum of Natural History P2004/4141-50	2004-10-06		
Background	5242	Krageholmssjön	Sediment	0-2 cm	2006-11-23		
Background	5241	Lilla Öresjön	Sediment	0-2 cm	2006-11-23		
Background	5240	Övre Skärsjön	Sediment	0-2 cm	2006-11-23		
Background	5243	Krageholmssjön	fish	perch P2006/2250-53 Swedish Museum of Natural History	2006-10-30		
Background	5244	Lilla Öresjön	fish	Perch P2006/1824-23 Swedish Museum of Natural History	2006-10-31		
Background	5245	Övre Skärsjön	fish	Perch P2006/1573-78 Swedish Museum of Natural History	2006-10-31		
Point sources		Stenungsund	Air		06-11-02 - 12-01	6444993	1266406
Point sources		Stenungsund	Air		07-01-03 - 02-01	6444993	1266406
Point sources		Stenungsund	Air		07-03-02 - 04-02	6444993	1266406
Point sources	5208	Stenungsund, A5	Sediment	0-2 cm	2006-10-25	6447870	1264882
Point sources	5209	Stenungsund, A8	Sediment	0-2 cm	2006-10-25	6446760	1264051
Point sources	5210	Stenungsund, F2	Sediment	0-2 cm	2006-10-25	6448959	1265181
Point sources	5211	Stenungsund, A1	Sediment	0-2 cm	2006-10-25	6446247	1264535
Point sources	5212	Stenungsund, D7	Sediment	0-2 cm	2006-10-25	6448098	1264879
Point sources	5213	Stenungsund, E1	Sediment	0-2 cm	2006-10-25	6446077	1253472
Point sources	5214	Stenungsund A1	fish	Eelpout, ca 5 individuals	2006-10-25	6447568	1265342
Point sources	5215	Stenungsund D7	fish	Eelpout, ca 5 individuals	2006-10-25	6448094	1264879
Point sources	5216	Stenungsund E1	fish	Eelpout, ca 5 individuals	2006-10-25	6446071	1263467

Category	Sample ID	Site	Matrix	Notes	Sampling date	X(RT90)	Y(RT90)
Point sources		Gislaved, Mossarp 1	Air		2006-11-09 - 12-07	N57°17.19'	E13°34.48'
Point sources		Gislaved, Mossarp 2	Air		06-12-07 - 12-21; 07-01-18 - 02-01	N57°17.19'	E13°34.48'
Point sources		Gislaved, Mossarp 3	Air		070201-070302	N57°17.19'	E13°34.48'
Diffuse	5224	Stockholm, Henriksdal STP	Sludge	644 000 p e	November 2006		
Diffuse	5221	Göteborg, Ryaverket STP	Sludge	605 000 p e	November 2006		
Diffuse	5226	Eslöv, Ellinge STP	Sludge	126 000 p e	November 2006		
Diffuse	5223	Alingsås, Nolhaga STP	Sludge	24 000 p e	November 2006		
Diffuse	5222	Floda STP	Sludge	9 800 p e	November 2006		
Diffuse	5225	Bollebygd STP	Sludge	2 200 p e	November 2006		
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		2006-11-20 - 12-19	6579403	1628272
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		2007-01-19 - 02-16	6579403	1628272
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		2007-02-16 - 03-16	6579403	1628272
Diffuse	5287	Stockholm Stora Essingen	Sediment	0-2 cm, depth 27.7 m	2006-12-05	6579263	1623658
Diffuse	5288	Stockholm Årstaviken	Sediment	0-2 cm, depth 7.6 m	2006-12-05	6578157	1628321
Diffuse	5296	Stockholm Riddarfjärden	Sediment	0-2 cm, depth 19.2m	2006-12-05	6580155	1627284
Diffuse	5526	Stockholm Riddarfjärden	fish	perch	2005-11-24		
Diffuse	5527	Stockholm Stora Essingen	fish	perch	2005-11-24		
Diffuse	5528	Stockholm Årstaviken	fish	perch	2006-12-06		
Human exposure	4093		Food-stuffs	Fish	National food administration F0500272, Fish Slurry 4		
Human exposure	4101		Food-stuffs	Dairy products	National food administration M0500034, Dairy Slurry 5		
Human exposure	4102		Food-stuffs	Dairy products	National food administration M0500035, Dairy Slurry 5		
Human exposure	4125		Food-stuffs	Vegetables	National food administration V0500041, Vegetables Slurry 10		
Human exposure	4126		Food-stuffs	Vegetables	National food administration V0500042, Vegetables Slurry 10		
Human exposure	4129		Food-stuffs	Cooking fats	National food administration V0500042, Vegetabilier Slurry 10		
Human exposure	5382		Urine	woman, age 34	December 2006		
Human exposure	5383		Urine	woman, age 51	December 2006		
Human exposure	5384		Urine	woman, age 39	December 2006		

Category	Sample ID	Site	Matrix	Notes	Sampling date	X(RT90)	Y(RT90)
Human exposure	5385		Urine	woman, age 44	December 2006		
Human exposure	5386		Urine	woman, age 39	December 2006		
Human exposure	5387		Urine	woman, age 51	December 2006		

Table A 2. List of samples for phthalate analysis, regional sampling programme

County	Sample ID	Site	Matrix	Notes	Sampling date	X(RT90)	Y(RT90)
Värmland	4989	Karlstad, Sjöstad STP	Sludge	61637 p e.	2006-09-18	6587178	1371427
Värmland	4994	Kristinehamn, Fiskartorpet STP	Sludge	16300 p e.	2006-09-19	6578124	1401080
Värmland	5019	Arvika, Vik STP	Sludge	19500 p e.	2006-10-02		
Värmland	5011	Säffle STP	Sludge	15973 p e.	2006-09-25		
Värmland	4325	Strandmossen landfill, Kristinehamn	Sediment		05-11-01		
Västerbotten	5085	Örnsköldsvik, Bodum STP	Sludge		2006-10-19	7021300	1650194
Västernorrland	5116	Sundsvall, Tivoliverket STP	Sludge		2006-10-24	6921185	1578267
Örebro	5557	Askersund ARV	Sludge		2007-03-27		
Örebro	5067	Karslskoga, Aggerud STP	Sludge		2006-09-25		
Örebro	5123	Lindesberg STP	Sludge		2006-10-31		
Örebro	5127	Skebäcksverket STP	Sludge		2006-10-31		

Table A 3. List of results, national and regional sampling programme

Category/County	Sample ID	Site	Matrix	DW (%)	Unit	DEHA	DEHP	DINP	DIDP	DEP	DIBP	DBP	BBzP
Background		Råö-1	Air		ng/m3	<0.2	1.1	0.48	<0.25	<0.04	0.57	0.26	0.022
Background		Råö-2	Air		ng/m3	0.02	0.5	<0.25	<0.25	0.17	0.38	0.28	0.028
Background		Råö-3	Air		ng/m3	0.04	0.6	<0.25	<0.25	0.05	0.15	0.08	0.06
Background	5375	Gårdsjön	Fish		µg/kg LW	<5	15	<50	<50				
Background	5376	Gårdsjön	Fish		µg/kg LW	<5	<10	<50	<50				
Background	5654	Gårdsjön	Fish		µg/kg LW	<5	<10	<50	<50				
Background	4687	Tärnan	Fish		µg/kg LW	<5	<10	<50	<50				
Background	5243	Krageholmssjön	Fish		µg/kg LW	<5	<10	<50	<50				
Background	5244	Lilla Öresjön	Fish		µg/kg LW	5	20	<50	<50				
Background	5245	Övre Skärsjön	Fish		µg/kg LW	<5	<10	<50	<50				
Background	5242	Krageholmssjön	Sediment	6.5	µg/kg DW	<30	<40	<100	<100				
Background	5241	Lilla Öresjön	Sediment	5.3	µg/kg DW	<30	<40	<100	<100				
Background	5240	Övre Skärsjön	Sediment	11.1	µg/kg DW	<30	<40	<100	<100				
Point sources		Stenungsund	Air		ng/m3	0.2	2.1	0.78	0.28	0.26	2.6	0.99	0.11
Point sources		Stenungsund	Air		ng/m3	0.1	1.1	0.28	<0.25	0.13	0.87	0.28	0.039
Point sources		Stenungsund	Air		ng/m3	0.6	1.3	0.59	2.4	0.12	1.9	0.76	0.07
Point sources	5208	Stenungsund, A5	Sediment	34.6	µg/kg DW	200	120	130	190				
Point sources	5209	Stenungsund, A8	Sediment	48.3	µg/kg DW	68	82	<100	<100				
Point sources	5210	Stenungsund, F2	Sediment	38.3	µg/kg DW	<30	<40	<100	<100				
Point sources	5211	Stenungsund, A1	Sediment	32	µg/kg DW	160	160	220	190				
Point sources	5212	Stenungsund, D7	Sediment	31.4	µg/kg DW	400	200	230	320				
Point sources	5213	Stenungsund, E1	Sediment	30.1	µg/kg DW	520	200	240	360				
Point sources	5214	Stenungsund A1	Fish		µg/kg LW	23	26	<50	<50				
Point sources	5215	Stenungsund D7	Fish		µg/kg LW	<5	<10	<50	<50				
Point sources	5216	Stenungsund E1	Fish		µg/kg LW	<5	<10	<50	<50				
Point sources		Gislaved-1	Air		ng/m3	0.1	2.9	0.5	0.5	0.17	0.48	15	0.034
Point sources		Gislaved-2	Air		ng/m3	0.3	2.9	1.1	2.0	0.06	0.32	4.8	0.023
Point sources		Gislaved-3	Air		ng/m3	0.2	3.0	0.52	0.36	0.07	0.59	12	0.029
Diffuse	5224	Stockholm, Henriksdal STP	Sludge	25.8	µg/kg DW	<30	43000	48000	23000				
Diffuse	5221	Göteborg, Ryaverket STP	Sludge	27.2	µg/kg DW	<30	47000	61000	24000				
Diffuse	5226	Eslöv, Ellinge STP	Sludge	16.5	µg/kg DW	110	40000	38000	20000				

Category/County	Sample ID	Site	Matrix	DW (%)	Unit	DEHA	DEHP	DINP	DIDP	DEP	DIBP	DBP	BBzP
Diffuse	5223	Alingsås, Nolhaga STP	Sludge	22.3	µg/kg DW	<30	44000	44000	19000				
Diffuse	5222	Floda STP	Sludge	18.3	µg/kg DW	<30	36000	53000	16000				
Diffuse	5225	Bollebygd STP	Sludge	15.6	µg/kg DW	<30	67000	61000	19000				
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		ng/m ³	0.2	1.7	0.84	1.1	1.0	1.4	3.6	0.17
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		ng/m ³	0.4	1.3	0.66	2.3	1.2	1.3	2.1	0.12
Diffuse		Stockholm, Wollmar Yxkullsg. 25	Air		ng/m ³	0.3	1.4	0.89	5.5	1.1	1.3	2.5	0.12
Diffuse	5287	Stockholm Stora Essingen	Sediment	14.1	µg/kg DW	<30	1200	2000	1200				
Diffuse	5288	Stockholm Årstaviken	Sediment	13.5	µg/kg DW	<30	2800	3200	3400				
Diffuse	5296	Stockholm Riddarfjärden	Sediment	15.7	µg/kg DW	<30	1900	2000	1500				
Diffuse	5526	Stockholm Riddarfjärden	Fish		µg/kg FW	<5	<10	<50	<50				
Diffuse	5527	Stockholm Stora Essingen	Fish		µg/kg FW	<5	<10	<50	<50				
Diffuse	5528	Stockholm Årstaviken	Fish		µg/kg FW	<5	23	<50	<50				
Human exposure	4093		Food-stuffs		µg/kg FW	8.2	310	250	<50				
Human exposure	4101		Food-stuffs		µg/kg FW	20	270	<50	<50				
Human exposure	4102		Food-stuffs		µg/kg FW	40	250	<50	<50				
Human exposure	4125		Food-stuffs	25.3	µg/kg FW	91	1900	74	32				
Human exposure	4126		Food-stuffs	27.5	µg/kg FW	8.8	140	54	21				
Human exposure	4129		Food-stuffs		µg/kg FW	470	380	260	<100				
Human exposure	5382		Urine		µg/l	-	6.6	<50					
Human exposure	5383		Urine		µg/l	-	11	<50					
Human exposure	5384		Urine		µg/l	-	7.7	<50					
Human exposure	5385		Urine		µg/l	-	0.7	<50					
Human exposure	5386		Urine		µg/l	-	0.9	<50					
Human exposure	5387		Urine		µg/l	-	11	<50					
Regional samples													
Värmland	4989	Karlstad, Sjöstad STP	Sludge	33.8	µg/kg DW	<30	66000	57000	23000				
Värmland	4994	Kristinehamn, Fiskartorget STP	Sludge	25.8	µg/kg DW	<30	59000	37000	21000				
Värmland	5019	Arvika, Vik STP	Sludge	16.2	µg/kg DW	<30	42000	51000	25000				
Värmland	5011	Säffle STP	Sludge	33.8	µg/kg DW	<30	43000	40000	16000				
Värmland	4325	Strandmossen landfill, Kristinehamn	Sediment	19.6	µg/kg DW	<30	400	440	290				
Västerbotten	5085	Örnsköldsvik, Bodum STP	Sludge	33.8	µg/kg DW	<30	42000	45000	19000				
Västernorrland	5116	Sundsvall, Tivoliverket STP	Sludge	33.8	µg/kg DW	<30	65000	65000	51000				

Category/County	Sample ID	Site	Matrix	DW (%)	Unit	DEHA	DEHP	DINP	DIDP	DEP	DIBP	DBP	BBzP
Örebro	5557	Askersund ARV	Sludge	2.4	µg/kg DW	182	40000	43000	16000				
Örebro	5067	Karslskoga, Aggerud STP	Sludge	1.6	µg/kg DW	<30	80000	63000	29000				
Örebro	5123	Lindesberg STP	Sludge	21.5	µg/kg DW	<30	47000	39000	15000				
Örebro	5127	Skebäckverket STP	Sludge	30.6	µg/kg DW	<30	67000	60000	21000				