

Sources of phthalates and nonylphenoles in municipal waste water

A study in a local environment

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Data sheet

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1 Summary

The overall aim of the present study is to identify and evaluate the importance of sources of nonylphenoles and phthalates in waste water in a local environment.

The investigations were carried out in a Danish local community, Roskilde city and surroundings.

Nonylphenoles and phthalates were analysed in the waste water from different institutions and industries thought to be potential sources. These were: car wash centers, a hospital, a kindergarten, an adhesive industry and an industrial laundry.

Furthermore, analysis of the deposition in the area were carried out. This made it possible to estimate the contribution from all of these sources to the waste water as well as the role of long-range air transport. Two local rivers were analysed for comparison.

Finally, waste water inlet from the local water treatment plant, where the sources converge at a single point, were analysed.

A mass balance for each source was calculated in relation to the total mass flow into the waste water plant, making it possible to evaluate the absolute and relative importance of each type of source. The sources investigated accounted for about 12% of the influx of DEHP, the predominating phthalate, to the waste water plant. The order of importance of sources for this substance were the laundries, followed by deposition, car washes and hospital. For nonylphenoles and DiNP, the kindergarten and the car washes were the predominant sources. However, the kindergarten result is uncertain being based on only a single sample.

The deposition concentrations were very low compared to the waste water. The deposition rates showed a seasonal variation with a minimum occurring two months after the winter temperature minimum. Surprisingly, no influence of the wind speed and direction was indicated.

The concentrations in the rivers were on the same or lower level as the deposition.

The levels found agree well with other Danish studies in the cases where such data exist.

2 Introduction

In a previous investigation of primary pollutants in waste water, high concentrations of octyl-phthalates were found (Miljøstyrelsen 1994). After the publication of the study, this finding caused considerable alarm since some phthalates had been recognised as possibly oestrogenic, making them harmful to male reproduction, and possibly playing a role for breast cancer in women (Miljøstyrelsen 1995a). Some other phthalates are listed as possibly carcinogenic (Arbejdstilsynet 1997).

The sources of the phthalates were, at that time, not identified, but a possible source was believed to be water from washing of plastics containing softeners. This conjecture as well as the results were publicly challenged by the plastics industry, referring to privately financed unpublished studies. Furthermore, by that time phthalates had not been recognised as a significant pollutant in municipal waste water (Miljøstyrelsen 1985, Miljøstyrelsen 1990). However, Swedish investigations found phthalates in industrial waste water (Alvin 1990), supporting the Danish results.

In a subsequent follow-up study (Vikelsøe 1995), phthalates in high concentrations were found in washing water from new PVC-floors, indicating that washing of softened plastic in buildings might be a source of phthalates, particularly BBP and DEHP, in waste water. Since these early studies, several Danish investigations of phthalates in waste water and sewage sludge have been carried out, all confirming the presence of phthalates (Miljøstyrelsen 1995b, 1996a, 1997a & 1997b).

The question of the identity and relative importance of the sources remained, however. This is the overall aim of the present study.

A manageable approach is to investigate the emission of phthalates in the waste water from an array of industries and institutions believed to be possible sources. Limiting the investigations to a local community makes it possible to evaluate the absolute and relative importance of each source in that community. This approach has been used in the present investigation.

Roskilde city and surroundings was chosen as the site of the study, since this community for many reasons makes a representative Danish provincial city. This city is thus of average size with a typical number of residents, institutions and industry. The waste water is processed in a single water treatment plant, facilitating the overview of the total waste water flow.

During the present studies, an extensive development in the methods for sampling and analysis has taken place.

3 Analytical methods

3.1 Analytical method 1 used for car wash

Development

The method was a scaled-down, simplified and improved version of a method previously used for analysis of phthalates in waste water (Miljøstyrelsen 1995b, Vikelsøe & Johansen 1997). Thus, the use of dipentylphthalate as an internal standard (syringe spike) was abandoned, and deuterium labelled DnOP was introduced instead. The advantage of this procedure is that labelled phthalates can be discriminated from the unlabelled phthalates in the sample by the mass spectrometric analysis, thus avoiding interference on the internal standard from phthalates in the sample. It further makes it possible to check correct operation of the equipment during the GC/MS analysis. It was the intention to use several other isotope labelled phthalates also, but they could not be obtained in the time available (they were introduced in method 2).

Sampling

The samples were taken in a well collecting the washing water. A proportional sampler of make ISCO was used at a flow setting of 200 ml/min, operating during the whole washing sequence, which had a duration of 5-7 min. A volume of 1200-1700 ml was collected in 2 l glass bottles, which before use had been heat-treated 4 hours at 450 °C to remove contamination.

Immediately after sampling, the samples were brought to the laboratory, frozen using a horizontal rotation device (to reduce the risk of glass fracture), and stored frozen until analysed.

Extraction

After thawing at room temperature, a 250 ml sample was extracted by shaking in 3x25 ml dichloromethane at pH 10 in a separatory funnel. The combined extracts were washed by shaking with 75 ml 0.01 M HCl. The extract was concentrated to about 5 ml in a rotary vacuum evaporator, dried by anhydrous sodium sulphate, filtrated, evaporated to near dryness under N₂ and dissolved in 0,25 ml syringe spike solution containing deuterium-labelled DnOP, (Table 1). The sample was diluted 1/1331 = (1/11)³ in this solution before GC/MS analysis.

Table 1 Syringe spike solution for method 1

| Substance | Label | µg/ml |
|-----------------------------|----------------|-------|
| Di(n-octyl)phthalate (DnOP) | D ₄ | 0.1 |
| Solvent | n-Hexane | |

Blank

A volume of 250 ml of tap water was extracted as blank, using the same method. The blank was processed together with the samples, taking care that the same batches of chemicals, glassware etc. were

used. The blank was analysed in the same dilutions as the 13 samples (for an overview of blanks, see section 3.4).

3.2 Analytical method 2 used for car wash, hospital and industry

Development

Method 1 was modified by the introduction of extraction spikes. These are added before the extraction, and makes it possible to identify the phthalates in the sample, to calculate recovery and to correct the results for losses during extraction and other laboratory procedures. *The use of labelled spikes is a substantial improvement.* The amount of solvent relative to the sample was increased. The method was scaled further down, making it more cost-efficient, and the smaller size of glassware made it possible to bake all glassware used in an oven at 450°C to remove contamination. This was expected to reduce the blank, since many experiments had shown that the main problem was contamination of the glassware, and not the solvents, as described in section 3.4. Furthermore, the smaller sample size made it unnecessary to analyse highly diluted samples. This is an advantage, since it was noted that high dilutions tended to increase the blank (an overview of the blanks is given in section 3.4). Before routine use, the changes were tested in a series of experiments. In spite of the efforts to bring down the blank, it was still high. It was attempted to use this method for small rivers, but because of the blank, the detection limit was too high.

Sampling

Waste water from car wash was sampled as described in method 1, i.e. in the well inside the washing room using a proportional sampler. For the adhesive industry and the laundry, it was possible to take the samples directly in glass bottles. For the kindergarten and the hospital, where the wells were too deep or narrow, a stainless steel bucket was hoisted down, and the liquid decanted into the sampling bottles. In all cases the samples were collected in 2 l glass bottles heat-treated at 450°C. All samples were immediately brought to the laboratory, frozen on a horizontal rotating device, and stored frozen until analysed.

Extraction

After thawing at room temperature, the 100 ml sample was spiked with 1 ml extraction spike solution (Table 2), corresponding to an amount of 10 µg for each spike. The sample was extracted by shaking with 3x50 ml dichloromethane at pH 10 in a separatory funnel.

The combined extracts were washed by shaking with 150 ml 0.02 M HCl. The extract was concentrated to a few ml in a rotary vacuum evaporator, dried by anhydrous sodium sulphate, filtrated, evaporated to near dryness under N₂ and dissolved in 1 ml syringe

spike solution (Table 1). It was diluted 1/100 in this solution before GC/MS analysis

Table 2 Extraction spike solution for car-wash method 2

| Substance | Label | µg/ml |
|----------------------------|----------------|-------|
| Dibutylphthalate | D ₄ | 10 |
| Benzylbutylphthalate | | |
| Bis(2-ethylhexyl)phthalate | | |
| Solvent | Ethanol | |

Blanks

A volume of 100 ml of tap water was extracted as blank, using the same method, and taking the same precautions as mentioned for method 1. A blank was made for every 6 samples.

3.3 Analytical method 3 used for deposition and small rivers

Development

The blank value especially for dibutylphthalate and DEHP present in the previous methods makes them unsuited for deposition measurements, which requires the detection of very low concentrations. The attempts to reduce the blank by cleaning the glassware had proved unsuccessful, so a new approach was needed. It was decided to abandon the repeated use of the same glassware, and exclusively use new glassware heat-treated at 450 °C. The heat treatment was absolutely necessary, since even new glassware contains significant amounts of especially DBP. The contact with chemicals and glassware was reduced as far as possible, hence the pH adjustment and the dilute acid-wash were omitted, and the use of large or difficult-to-clean glass equipment such as separatory funnels or rotary vacuum evaporators was abandoned. The extraction was carried out directly in the sampling flask, and the only other glassware in contact with the samples were pasteur pipettes, 20 ml vials, and the injection vials and inserts for the autosampler. This required that the samples were extracted *only once*. However, since the final results were calculated in relation to the extraction spikes, extraction losses were compensated, thus eliminating systematic errors. Because of the high-resolution mass spectrometric analysis, no interferences from other substances were present, making it possible to analyse the uncleaned samples with good results. Furthermore, the use of tap water in blanks was abandoned, since it was by then firmly established that tap water in the laboratory contained about 10 µg/l DEHP (Table 4). Instead empty glassware was extracted for the blanks (actual blank values and a discussion are given in section 3.4).

Sampling

The small rivers were sampled by means of glass beakers, collecting 1.2 - 1.4 l in 2 l glass bottles. The deposition was sampled in

bulk i.e. passively collected in funnels. This method is simple, cheap and reliable, as no electronics or moving parts are required. Furthermore, it is possible to clean and bake the all-glass equipment in the laboratory, leading to a low blank, which as previously noted is of the utmost importance. In spite of these virtues, a known drawback of the bulk method is a tendency to underestimate the contribution from the dry deposition, and from the snow deposition in the winter.

The equipment used is described in *Cleemann et al 1995*. The samplers consisted of 2 l glass bottles equipped with 20 cm Ø glass funnels. The 4 samplers were mounted with the upper edges 1.7 m above the ground in a rectangular rack with east-west side length of 1.3 m and north-south side length of 1 m. The bottles were enclosed in black plastic cylinders to protect them from sunlight. The samplers were changed every 2 weeks.

Before use all glassware was heat-treated at 450 °C to remove contamination. After sampling and transportation to the laboratory, foreign objects such as leaves and insects were removed. In case of snow in the funnels, this was thawed and the melting water allowed to run into the bottles. The funnels were then removed and wrapped in aluminium foil, and the water in the bottles frozen on a horizontal rotating device. The bottles and funnels were stored in the freezing room until analysed.

Extraction

After thawing at room temperature the volume of water present in the sampling bottle was measured. A volume of 0.1 ml extraction spike solution (Table 2) was added directly in the bottle which was subsequently shaken and left for 15 min to equilibrate the extraction spikes with the water and the glass surfaces. The amount of spike was in this case only 0.1 µg anticipating lower analyte concentration. A volume of 100 ml dichloromethane was then spiked with 0.1 ml syringe spike solution (Table 3), containing 1 µg of spike. For deposition samples, the funnel was placed in the bottle, and rinsed with this solution. The sample was then extracted by shaking 15 min in the bottle with the solution. In this way the syringe spike is present during the extraction, contrary to normal practice where it is added after the extraction.

Table 3 Syringe spike solution for method 3

| Substance | Label | µg/ml |
|-----------------------------|----------------|-------|
| Di(n-octyl)phthalate (DnOP) | D ₄ | 10 |
| Solvent | n-Hexane | |

The bottle was left until the phases were separated. A sub-extract of about 10 ml of the lower phase was transferred to a 20 ml glass vial by means of a pasteur pipette. This approximate pipetting of the sub-extract does not impair precision, since all spikes are pres-

ent. Thus the use of volumetric pipettes, which are difficult to bake out, is avoided. The sub-extract was concentrated under N₂ to about 1 ml and analysed directly by GC/MS.

Blanks

Test experiments with this method showed that tap water of the laboratory contained DEHP, making it unsuited for blank. Instead an empty bottle and a funnel were extracted (empty blanks). A blank was made for every 6 samples. The actual blanks are described in the following section 3.4.

3.4 Overview of blanks for the methods

Table 4 gives an overview of the blanks for the 3 different methods. In the upper part of the table, the blanks are given in µg/sample, and in the lower part in µg/l. For the blanks in multiple determinations (n>1) in methods 2 and 3, the average, standard deviation and coefficient of variation are given.

Table 4 Overview of blanks for the 3 different methods

| Met | Type | cal | n | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | ml | Dilut. |
|--|------|-----|---|------|------|------|------|--------|-------|------|------|-------|-----|--------|
| <i>Average & standard deviation of amounts, µg/sample. CV, %</i> | | | | | | | | | | | | | | |
| 1 | TW | | 1 | 30 | | 108 | | | 29 | | | na | 250 | 1000 |
| 2 | TW | avg | 9 | 5 | 2 | 79 | 0.03 | 0.5 | 3 | 0.2 | 0.1 | 10 | 100 | 100 |
| | | std | 9 | 9 | 2 | 18 | 0.06 | 0.6 | 1 | 0.2 | 0.3 | 16 | 100 | |
| | | CV | 9 | 176 | 119 | 22 | 205 | 130 | 36 | 126 | 199 | 155 | 100 | |
| 2 | TW | | 1 | | 38 | 436 | 2 | 3 | 156 | | | 1352 | 100 | 10000 |
| 3 | Em | avg | 3 | 0.04 | 0.12 | 0.12 | | 0.12 | 0.62 | 0.27 | | | | 1 |
| | | std | 3 | 0.03 | 0.17 | 0.03 | | 0.0004 | 0.10 | 0.01 | | | | |
| | | CV | 3 | 68 | 141 | 21 | | 0.3 | 16 | 4 | | | | |
| 3 | TW | | 1 | 0.70 | 0.12 | 0.25 | | 0.48 | 9.4 | 0.27 | | | 800 | 1 |
| <i>Average & standard deviation of concentrations, µg/l</i> | | | | | | | | | | | | | | |
| 1 | TW | | 1 | 119 | | 434 | | | 115 | | | na | 250 | 1000 |
| 2 | TW | avg | 9 | 53 | 16 | 794 | 0.3 | 5 | 27 | 2 | 1 | 103 | 100 | 100 |
| | | std | 9 | 93 | 18 | 179 | 0.6 | 6.0 | 10 | 1.9 | 2.6 | 160 | 100 | |
| 2 | TW | | 1 | | 377 | 4363 | 18 | 32 | 1561 | | | 13515 | 100 | 10000 |
| 3 | Em | avg | 3 | 0.05 | 0.15 | 0.15 | | 0.15 | 0.77 | 0.34 | | | 800 | 1 |
| | | std | 3 | 0.04 | 0.22 | 0.03 | | 0.00 | 0.13 | 0.01 | | | 800 | |
| 3 | TW | | 1 | 0.88 | 0.15 | 0.31 | | 0.60 | 11.70 | 0.34 | | | 800 | 1 |

TW = Tapwater Em = Empty A fictitious volume of 800 ml (close to the deposition average, marked in *italics*) has been used to calculate the concentration of the empty blank

Blanks, amount µg/sample

Assuming that most of the contaminating phthalates of the glassware and chemicals are transferred to the sample, the amount of phthalates present during the laboratory processing will be approximately constant. Thus µg/sample is the unit best suited to compare blanks of the methods.

Comparing method 1 in 1000 dilution with method 2 in 100 dilution in $\mu\text{g}/\text{sample}$, it is seen that method 2 has about 30 times lower DEHP blank, indicating that the washing, rinsing and heat-treating of the glassware in method 2 is effective for removal of this substance. Unfortunately, the DBP blank is only slightly reduced. It is further noted that method 2 in 10000 dilution has much higher blanks than in 100 dilution. This is probably due to slight contamination of the volumetric glassware and syringe spike used during the dilution, which has a large impact on the final result since this is obtained by multiplication of raw result by 10000. Of course, such high dilutions are necessary only for very concentrated samples to avoid saturation of the MS-signal. These high dilutions necessary in such cases is a drawback of the highly sensitive mass spectrometer used for the analysis, in spite of its many other virtues.

As can be seen, the method 3 undiluted empty blank is much lower, being only $0.4 \mu\text{g}/\text{sample}$ for DBP and $0.9 \mu\text{g}/\text{sample}$ for DEHP. *The efforts to lower the blank by introducing method 3 has thus been successful.* The tapwater measured by this method showed a DEHP amount of $9 \mu\text{g}/\text{sample}$, much higher than the empty blank for this substance. It must therefore be concluded that this DEHP originates from the tapwater, which is supplied to NERI by a water works owned by the neighbour institution. Because of this discovery, the use of tapwater for blanks was abandoned.

Blanks concentration, $\mu\text{g}/\text{l}$

To make comparisons with the concentrations measured in the project, the blanks are recalculated in the concentration units $\mu\text{g}/\text{l}$ by division with the volume of the water extracted. Looking at the blanks given in $\mu\text{g}/\text{l}$, the situation is not so favourable for method 2 compared to method 1 because of the lower volume of method 2. For DBP, the blank is doubled, but for DEHP it still is about 4 times lower. For the empty blank of method 3, the fictitious volume of 800 ml (marked in *italics*) is used to calculate the blank. These concentrations are strictly speaking fictitious, having no direct chemical meaning, but are useful for comparison with the results. As can be seen, this is roughly 2000 times lower than the method 2 blank for DBP, and about 30 times lower for DEHP, showing the very substantial improvement of method 3. Finally the tapwater measured by method 3 is seen to contain about $12 \mu\text{g}/\text{l}$ of DEHP, the phthalate found in highest concentration in that matrix. It would clearly be impossible to measure this low concentration accurately by either methods 1 or 2.

Search for blank sources

An extensive search to locate the DBP source was carried out during the methods development work, as described in the appropriate sections. In the beginning, the solvents used (especially dichloromethane and n-hexane) were suspected, but after many tests they could be cleared completely. However, DBP was found on the outside of the solvent bottles and even in newly purchased glass vials in varying amounts depending on the supplier. Reused

glassware was found always to contain DBP in significant amounts, even if machine washed, solvent rinsed and heat-treated. As mentioned above, the tapwater in the laboratory contained DEHP, in fact in much higher concentrations than deposition water as shown in the results section. In spite of considerable efforts, the attempts to locate a main source for DBP remained unsuccessful. The conclusion must be that phthalates, and especially DBP, seem to be ubiquitous in the laboratory building.

Limit of determination

The limit of determination of the methods is dominated by the uncertainty of the blank, since the blank is subtracted from the raw data to give the final result. Hence the limits of determination can be calculated as the standard deviation of the blank, given on the 1 sigma level in Table 5. The 1 sigma level has been chosen in order to retain as many low-level data as possible, since the aim of the investigation is to compile a mass balance (and not to check limit values). In case of multiple blank determinations, the standard deviation of the average (equal to the standard deviation divided by the squareroot of n) is used. For substances which are not detected in the blank, as for example DPP, the limit of determination depends on the mass spectrometric detection limit, which is much lower. This is routinely calculated by the software of the mass spectrometer from the signal to noise ratio of the relevant mass track and the response factor of the corresponding standard (see section 3.5). For method 1 and the highly diluted samples of method 2, only 1 blank was carried out. In these cases, the standard deviation is estimated from that blank, assuming the same coefficient of variation as found for method 2. Note that the unit for method 3 concentrations is $\mu\text{g}/\text{m}^3$.

Table 5 Limits of determination for the different methods, dilutions and units

| Met | Unit | Dilut. | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP |
|-----|-----------------------------------|--------|------|------|-----|------|-----|------|------|------|-------|
| 1 | $\mu\text{g}/\text{l}$ | 1000 | 210 | 7 | 98 | 0.2 | 2 | 41 | 0.8 | 1.0 | na |
| 1 | mg/wash | 1000 | 29 | 1 | 14 | 0.03 | 0.3 | 5.8 | 0.1 | 0.1 | na |
| 2 | $\mu\text{g}/\text{l}$ | 100 | 31 | 6 | 60 | 0.2 | 2 | 3 | 0.6 | 0.9 | 53 |
| 2 | mg/wash | 100 | 4 | 0.9 | 8 | 0.03 | 0.3 | 0.5 | 0.1 | 0.1 | 7 |
| 2 | $\mu\text{g}/\text{l}$ | 10000 | 3017 | 448 | 982 | 38 | 41 | 565 | 63 | 84 | 20912 |
| 3 | $\mu\text{g}/\text{m}^3$ | 1 | 25 | 153 | 23 | 4 | 0.3 | 90 | 11 | 21 | 106 |
| 3 | $\mu\text{g}/\text{m}^2/\text{y}$ | 1 | 9 | 53 | 8 | 1 | 0.1 | 31 | 4 | 7 | 37 |

As can be seen, the limits of determination varies considerably between methods and dilutions. The determination limits are also given in the appropriate results tables in abbreviated form in the results chapter.

3.5 Analysis by gaschromatography/mass spectrometry (GC/MS)

Standard solutions

Standard solutions are used for quantification and identification, (Table 6). They are analysed by GC/MS at regular intervals (i.e. for every 5 samples). They are called external, since they are analysed separately from the samples.

Table 6 Phthalate standard solutions for GC/MS

| Substance | Acronym | µg/ml low | µg/ml med | µg/ml high | Type | Ref met. 1 | Ref met. 2 &3 |
|---|----------------------|--------------|--------------|---------------|------|---------------|---------------------|
| Nonylphenol | NP | 0.01 | 0.1 | 1 | | | 1 |
| Nonylphenol diethoxylate | NPDE | 0.05 | 0.5 | 5 | | | 1 |
| Dibutylphthalate | DBP | 0.01 | 0.1 | 1 | | | 1 |
| Dipentylphthalate | DPP | 0.01 | 0.1 | 1 | | | 1 |
| Benzylbutylphthalate | BBP | 0.01 | 0.1 | 1 | Ana | 4 | 2 |
| Di-(2ethylhexyl)-phthalate | DEHP | 0.01 | 0.1 | 1 | | | 3 |
| Di-(n-octyl)-phthalate | DnOP | 0.01 | 0.1 | 1 | | | 3 |
| Di-(n-nonyl)phthalate | DnNP | 0.01 | 0.1 | 1 | | | 3 |
| Di-("iso"-nonyl)phthalate | DiNP | 0.01 | 0.1 | 1 | | | 3 |
| D ₄ -Dibutylphthalate | D ₄ -DBP | | | | | | 1 |
| D ₄ -Benzylbutylphthalate | D ₄ -BBP | 0.1 | 0.1 | 0.1 | Esp | | 2 |
| D ₄ -Bis-(2ethylhexyl)-phthalate | D ₄ -DEHP | | | | | | 3 |
| D ₄ -Di-(n-octyl)-phthalate | D ₄ -DnOP | 0.1 | 0.1 | 0.1 | Ssp | 4 | 4 |
| Solvent for standard, method 1 & 2 | n-Hexane | | | | | | |
| Solvent for standard, method 3 | Dichloromethane | | | | | | |

The Type column refers to: Ana = Analyte, Esp = Extraction spike, Ssp = Syringe spike

The Ref columns indicates the spikes used for calculation of the results for each analyte.

Thus for method 1, all analytes are calculated from the syringe spike (no 4).

For method 2 & 3, e.g. DBP and DPP are calculated from D₄-DBP (Ref 1), BBP from D₄-BBP (Ref 2) etc.

Gaschromatography

Hewlett-Packard 5890 series II gas chromatograph

Injection:

2 µl split/splitless 270°C, purge closed 40 sec.

Pre-column:

Chrompack Retention Gap. Fused silica, 2.5 m x 0.32 mm i.Ø,

Column:

J&W Scientific DB5-MS. Fused silica, 30 m x 0.252 mm i.Ø, crosslinked phenyl-methyl silicone 0.25 µm film thickness

Carrier gas:

Helium, pressure 120 Kpa

Temperature programs:

Method 1 & 2 40 sec at 80°C, 10°C /min to 290°C, 15 min at 290°C

Method 3 40 sec at 50°C, 10°C /min to 290°C, 15 min at 290°C

Resolution: 10.000 (10% valley definition)

Ionisation: Electron impact 50 EV, ion source temperature 270°C

Interface: 290°C direct to ion source

Calibration gas: Perfluoro-kerosene (PFK)

Scan: 0.6 sec per scan in Selected Ion Monitoring (SIM) mode (Table 7).
(about 0.1 sec per ion)

Table 7 Masses for high resolution MS- analysis

| Substance | Mass |
|---|----------|
| Nonylphenoles | 135.0809 |
| Unlabelled phthalates | 149.0239 |
| D ₄ -labelled phthalates (spikes). | 153.0490 |
| Lock mass | 130.9920 |

The lock mass is a line in the PFK-spectrum used to compensate for random variations in the magnetic field of the instrument.

In Fig 1 to Fig 3 are shown examples of chromatograms.

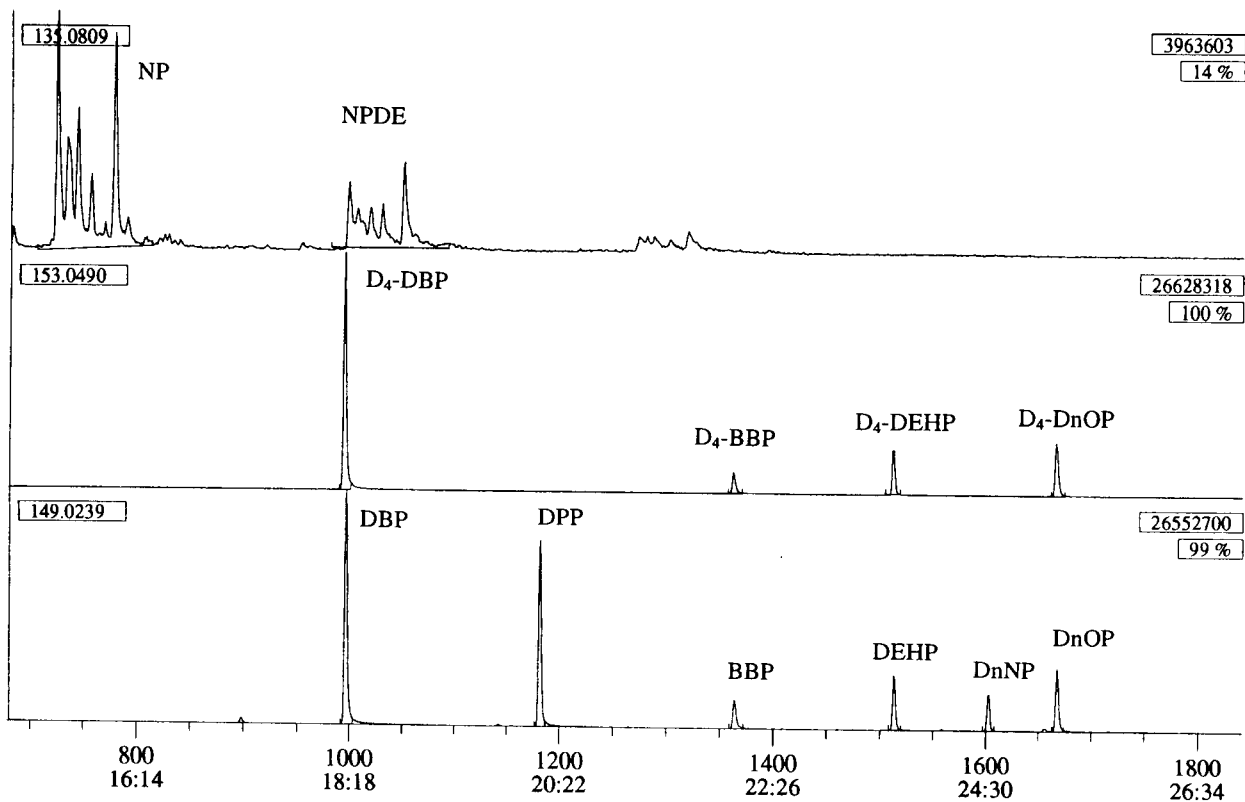


Fig. 1 Chromatograms for CG/MS analysis of the external standard with concentration 0.1 µg/ml. The upper mass track shows nonylphenoles, the middle track labelled phthalates (spikes) and the lower track unlabelled phthalates.

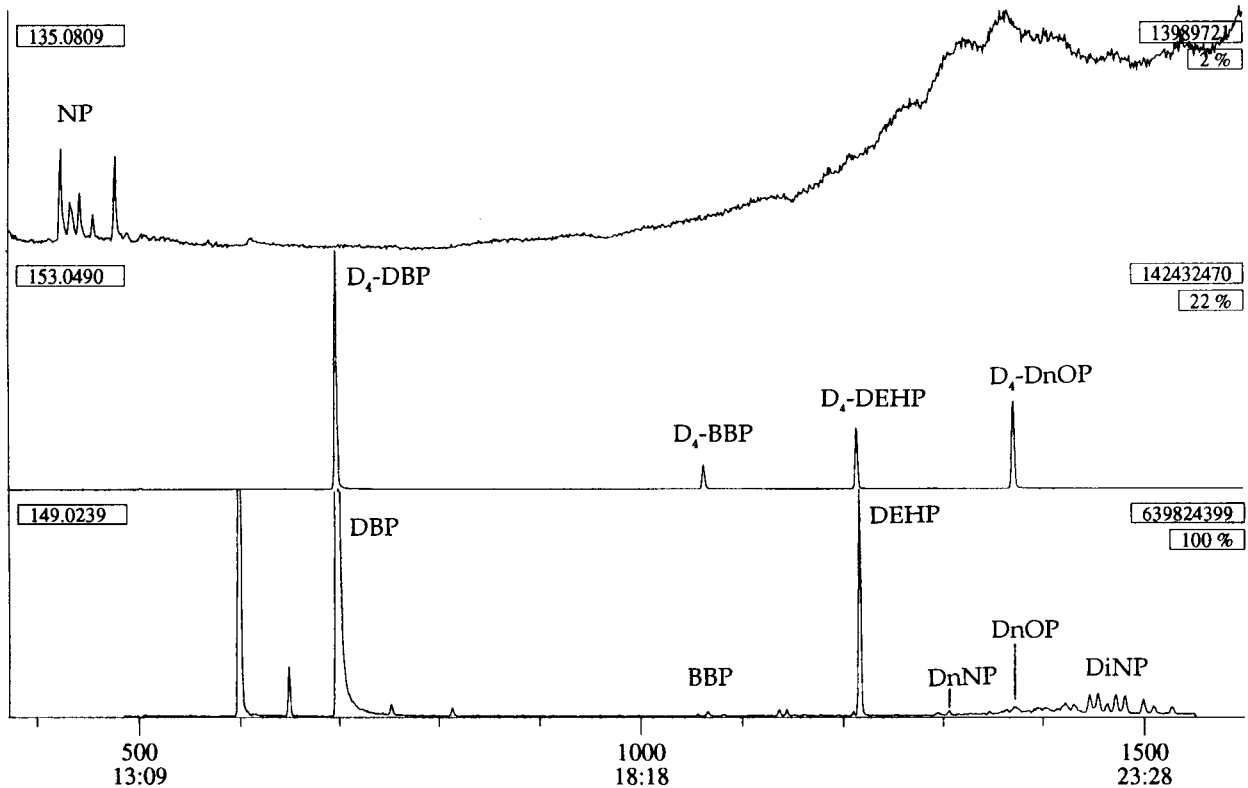


Fig. 2 Chromatograms for GC/MS analysis of a car wash waste water sample (NERI No. 7.0010). The NP group of peaks are present on the upper track. On the middle track, all peaks from spikes are seen. On the lower track, all phthalate peaks, except DPP, are present. The DiNP group is clearly seen.

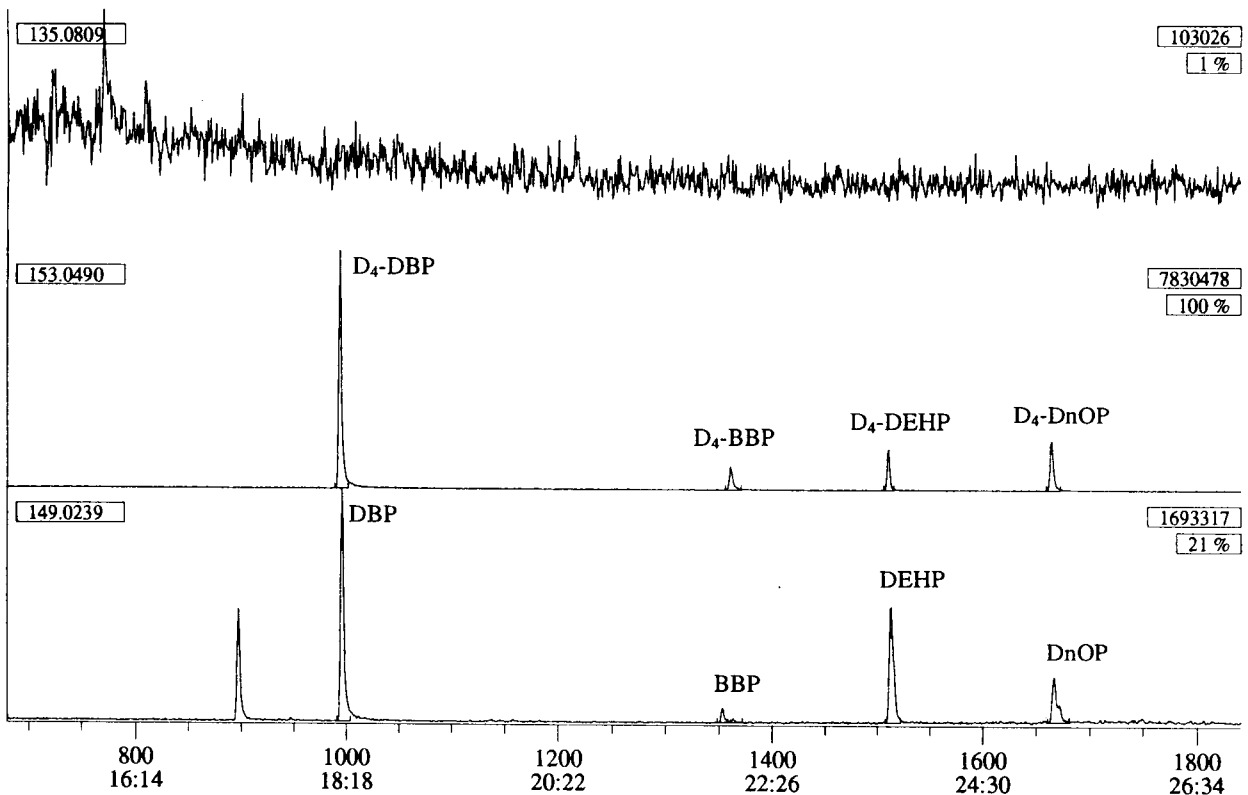


Fig. 3 Chromatograms for GC/MS analysis of a deposition sample (NERI No 7.0141). No peaks are present on the upper NP track. On the middle track, all spike peaks are seen. On the lower phthalate track, the DBP and DEHP peaks are the largest, but also BBP and DnOP peaks are present.

3.6 Calculations

Analytical method 1

For each substance a response factor is calculated from the GC/MS analysis of the external standard according to the formula:

$$R_i = \frac{C_{ss}}{C_{is}} \cdot \frac{A_{is}}{A_{ss}}$$

where:

- R_i = Response factor for substance i
- C_{is} = Concentration of substance i in the external standard
- C_{ss} = Concentration of syringe spike in external standard (0.1µg/ml)
- A_{is} = Area for analyte i in the external standard
- A_{ss} = Area for syringe spike in the external standard

The concentrations in the unknown samples are then calculated according to the formula:

$$C_{ip} = \left(\frac{100 \cdot D \cdot V_u}{R\%_e} \cdot \frac{C_{su} \cdot A_{iu}}{R_i \cdot A_{su}} - C_b \right) \cdot \frac{1}{M_p}$$

where:

- C_{ip} = Concentration of substance i in the unknown sample
 - D = Dilution factor (1331)
 - V_u = Volume of sample dissolved in syringe spike (0.25 ml)
 - $R\%_e$ = Recovery of corresponding 1) extraction spike 2)
 - C_{su} = Concentration of syringe spike in the sample (0.1µg/ml)
 - A_{iu} = Area for substance i in the unknown
 - R_i = Responsefactor for substance i (calculated above)
 - A_{su} = Area for syringe spike in the unknown
 - C_b = Average concentration of corresponding blanks (calculated according to first term of formula)
 - M_p = Amount of unknown sample extracted (250 ml)
- 1) Given in Ref column in Table 5
 - 2) The recovery used is the average from results of method 2.

The 2 methods should theoretically give the same recoveries, since the extraction procedures are comparable.

The result is thus first calculated as µg/sample, and the average corresponding blanks subtracted also in µg/sample. This procedure is adopted since the amount of contamination from glassware and chemicals per sample is approximately constant. The difference is then divided by the amount of water extracted to give the final result.

In this case, the extraction spikes are used as reference for the analytes. For each analyte a response factor is calculated from the GC/MS analysis of the external standard according to the formula:

$$R_i = \frac{C_{es}}{C_{is}} \cdot \frac{A_{is}}{A_{es}}$$

where:

| | | |
|----------|---|--|
| R_i | = | Response factor for analyte i |
| C_{is} | = | Concentration of analyte i in the external standard |
| C_{es} | = | Concentration of the corresponding 1) extraction spike |
| A_{is} | = | Area for the analyte i for the external standard |
| A_{es} | = | Area of the corresponding 1) extraction spike |

1) The correspondences between analytes and extraction spikes are given in Table 5 in the Ref-columns.

The concentrations in the unknown samples are then calculated. The extraction spike areas are used as a reference for the analytes, compensating for extraction and other losses, according to the formula:

$$C_{ip} = \left(D \cdot V_u \cdot \frac{C_{eu} \cdot A_{iu}}{R_i \cdot A_{eu}} - C_b \right) \cdot \frac{1}{M_p}$$

where:

| | | |
|----------|---|---|
| C_{ip} | = | Concentration of analyte i in the unknown sample |
| D | = | Dilution factor (x dilution) |
| V_u | = | Volume of sample dissolved in syringe spike |
| C_{eu} | = | Concentration of corresponding extraction spike in the sample |
| A_{iu} | = | Area of analyte i in the unknown |
| R_i | = | Response factor for analyte i (calculated above) |
| A_{eu} | = | Area for corresponding extraction spike in the sample |
| C_b | = | Average concentration of corresponding blanks (calculated according to first term of formula) |
| M_p | = | Amount of unknown sample extracted |

Recovery

The recovery is calculated for extraction spike e according to the formula:

$$R\%_e = 100 \cdot \frac{A_{eu} \cdot C_{su}}{A_{su} \cdot C_{eu}} \cdot \frac{A_{ss} \cdot C_{es}}{A_{es} \cdot C_{ss}}$$

where:

| | | |
|----------|---|---|
| $R\%_e$ | = | Recovery % of extraction spike e in sample |
| A_{eu} | = | Area of extraction spike e for sample |
| C_{eu} | = | Nominal (added) concentration of extraction spike e in sample |
| A_{su} | = | Area of syringe spike for sample |
| C_{su} | = | Concentration of syringe spike in the sample |
| A_{es} | = | Area of extraction spike e for standard |
| C_{es} | = | Concentration of extraction spike e in standard |
| A_{ss} | = | Area of syringe spike for standard |
| C_{ss} | = | Concentration of syringe spike in standard |

4 Samples

The investigation was concentrated in areas in or near by Roskilde city. An overview of the types and number of samples is shown in Table 8. The source samples are taken from sites expected to be potential point sources to phthalate esters in the environment such as institutions and industry.

Table 8 Overview of samples

| Sampling type and site | n |
|--|-----|
| <i>Car wash</i> | |
| Site A, reverse osmosis water system | 14 |
| Site B, conventional water system | 12 |
| <i>Institutions</i> | |
| Roskilde Municipal Hospital | 6x2 |
| Integrated institution for babies, children and young handicapped (kindergarten) | 2 |
| <i>Industry</i> | |
| Adhesives Industry located in Herlev, a town far from Roskilde | 2x2 |
| Industrial laundry | 2 |
| <i>Small rivers</i> | |
| Maglemose Å & Kildemose Å 7km N of Roskilde | 2 |
| Hove Å 8 km N of Roskilde | 2 |
| <i>Deposition</i> | |
| Lille Valby meteorological station | 8x4 |
| <i>Wastewater treatment plant (WTP)</i> | |
| Inlet. Receives water from the Roskilde municipal area | 2x5 |
| Outlet. Discharges into Roskilde Fjord (not reported in present report) | 2x5 |

The waste water treatment plant samples makes it possible to estimate the total flow of nonylphenoles and phthalates in the sewer system of Roskilde, since the city has only this plant. The deposition samples are included in the investigation to evaluate the significance of nonylphenoles and phthalates carried into the waste water system from air sources, and to take this contribution into account in the total phthalate mass flow from local sources. The deposition is further assumed to give an indication of the role of long range air transport. The deposition is sampled as bulk. The deposition at Lille Valby may not be fully representative for the Roskilde area because of the distance of about 8 km from the city centre. The small rivers are included in the investigations for comparison to the deposition. They receive water from a rural area, and flow into Roskilde Fjord. The adhesives industry (glue manufacturer) is located in Herlev, a town without waste water system common with Roskilde, and is therefore exclusive the Roskilde area samplings

The data for waste water samples from car wash are summarised in Table 9.

Table 9 Waste water samples from car wash

| NERI no. | Sampling date | Wash Site | Wash progr | Car Model | Built year | In |
|----------|---------------|-----------|------------|-----------|------------|-----|
| 6.1044 | 96-11-17 | A | BU | HA | 1993 | Eur |
| 6.1045 | 96-11-17 | A | BU | EA | 1983 | Eur |
| 6.1046 | 96-11-17 | A | BUW | AA | 1994 | Eur |
| 6.1047 | 96-11-17 | A | BUW | EC | 1986 | Eur |
| 6.1048 | 96-11-17 | A | BUW | GA | 1994 | Eur |
| 6.1049 | 96-11-17 | A | BU | BA | 1995 | Eur |
| 6.1050 | 96-11-17 | A | BU | KA | 1989 | Jap |
| 6.1051 | 96-11-17 | A | BUW | CB | 1993 | Eur |
| 6.1052 | 96-11-17 | A | BUW | EB | 1995 | Eur |
| 6.1053 | 96-11-17 | A | BUW | JA | 1996 | Jap |
| 6.1054 | 96-11-17 | A | BU | EB | 1994 | Eur |
| 6.1055 | 96-11-17 | A | BU | BB | 1987 | Eur |
| 6.1056 | 96-11-17 | A | BUW | FB | 1996 | Eur |
| 6.1080 | 96-11-17 | A | BUW | FB | 1996 | Eur |
| 7.0002 | 97-01-04 | B | BU | ED | 1984 | Eur |
| 7.0003 | 97-01-04 | B | BU | L | 1987 | Jap |
| 7.0004 | 97-01-04 | B | BUW | L | 1993 | Jap |
| 7.0005 | 97-01-04 | B | BUW | IA | 1987 | Eur |
| 7.0006 | 97-01-04 | B | BU | FA | 1996 | Eur |
| 7.0007 | 97-01-04 | B | B | HA | 1996 | Eur |
| 7.0008 | 97-01-04 | B | B | LA | 1993 | Jap |
| 7.0009 | 97-01-04 | B | BU | EB | 1996 | Eur |
| 7.0010 | 97-01-04 | B | BU | DA | 1987 | Eur |
| 7.0011 | 97-01-04 | B | BU | CA | 1994 | Eur |
| 7.0012 | 97-01-04 | B | BU | K | 1995 | Jap |
| 7.0013 | 97-01-04 | B | B | CA | 1992 | Eur |

B = Basic wash U = Undercar rinse W = Wax treatment
 Car model code: First letter manufacturer, second letter car model

The samples were taken at the car wash station in the well collecting the washing water in the washing room. This position close to the cars was chosen since it was the intention to obtain samples representative of the individual cars. Downstream of the collecting well a waste water train was located, consisting of a sand trap, a reservoir and an oil separation trap. Hence, considerable mixing of the water from the individual washing tests occurs in the train. The purpose of the sand trap is to collect sand and other particles. The water for the undercar rinse was pumped from the reservoir, and the oil trap discharged the waste water into the municipal sewer system. It was not possible to take samples at this position due to poor accessibility.

At site A a reverse osmosis water treatment system was installed to desalt the water for the final rinse. This reduced the detergent

consumption according to the installing firm. Site B used a conventional water system.

For each test the type of washing programme was noted. In Table 9, "B" stands for basic wash, "U" for undercar rinse and "W" for wax treatment. The majority of the customers chose the "Gold" program comprising all these features. The duration of the washing sequence amounted to 4 to 7 min depending on the type of washing program, as the undercar rinse as well as the wax treatment prolonged the duration with some minutes.

For each car, the manufacturer and model was noted, and the year of production was asked from the customer. It was intended also to include the type of anti-rust protection of the car underside in the data, since undercar protection with PVC in new cars is a suspected phthalate source. However, this was given up because the data were difficult to obtain.

Hospital

The Roskilde municipal hospital was chosen for the investigation. It is a comparable large institution treating about 25000 patients annually, employing about 2000 people. The hospital ground covers an area of about 0.05 km². It was the aim both to pinpoint the main source and to get representative samples for the overall waste water emission. One sampling site (position B) was located near the main medical treatment building complex at the X-ray department where a large phthalate emission was suspected. The two other sites chosen were located in the perimeter of the hospital grounds, at the physicians building and at a parking lot, respectively. Together, the three positions cover the total waste water emission from the hospital. Two samples were taken at each site.

Kindergarten

Kindergartens were suspected phthalate emitters since in some institutions the children are working with finger paint, which may contain phthalates. The paint is discharged directly into the sewer system after hand washing. The site investigated was chosen since they were working with finger paint. It is a so-called integrated institution for babies, children and young handicapped located in Roskilde. Also PVC-floors may be a source of phthalates during washing, but the building reportedly contained only a few m² of PVC in the lavatories, the other floors being covered with linoleum. Two samples were taken in a sewer well outside the buildings collecting the waste water from the whole institution. However, one sample was lost as the bottle disintegrated during freezing at the laboratory, leaving only one for analysis.

Industry

Industrial laundries were suspected of emitting nonylphenol-ethoxylates due to the use of detergents, and of phthalates being washed out of textiles. An industrial laundry in Roskilde was selected.

The adhesives industry was also a suspected phthalate emitter, since some of their products contain phthalates in large quantities. As no such industry is located in Roskilde, a manufacturer of glue and sealants in the town of Herlev (to the north of Copenhagen, about 30 km from Roskilde) was chosen. One sample was taken during normal operating conditions, whereas another was taken during a simulated spilling episode when cleaning a process tank (normally, the washing water from tank cleaning is recycled). The latter sample was included as a worst-case occurrence of the phthalate esters BBP and DEHP in waste water. In all cases the samples were taken in outlet wells collecting the wastewater just outside the buildings.

The data for the waste water samples from institutions and industry are given in Table 10. The NERI sampling numbers are for reference to the results.

Table 10 Waste water samples from institutions and industry

| NERI no. | Sampling date | Site | Position /episode |
|----------|---------------|--------------|--------------------|
| 6.1069 | 96-11-21 | Hospital | Parking lot |
| 6.1070 | 96-11-21 | Hospital | Parking lot |
| 6.1071 | 96-11-21 | Hospital | Treatment building |
| 6.1072 | 96-11-21 | Hospital | Treatment building |
| 6.1073 | 96-11-21 | Hospital | Physician building |
| 6.1074 | 96-11-21 | Hospital | Physician building |
| 6.1067 | 96-11-21 | Kindergarten | |
| 6.1007 | 96-11-04 | Adhesives | Simulated spill |
| 6.1008 | 96-11-04 | Adhesives | Normal operation |
| 6.1009 | 96-11-06 | Laundry | |
| 6.1010 | 96-11-06 | Laundry | |

Small rivers

To investigate the discharge into the Roskilde Fjord, a few samples were taken in small rivers. Maglemose Å (Å = small river) runs into the fjord 7 km and Hove Å 8 km to the north of Roskilde. In both rivers, the samples were taken in the river mouth and 5 m upstream, respectively.

Deposition

The deposition was sampled at Lille Valby meteorological station located near NERI, about 6 km to the north of Roskilde, about one km to the east of the fjord. The equipment described in the *Methods* section was deployed on a flat field to minimise air turbulence, which can lead to erroneous results. Four samples were taken simultaneous in each period, but only the north-east and north-west samples were analysed for phthalates. The data for these samples are given in Table 11.

The locations of the sampling sites are shown on the map Fig. 4 in Section 4.

Table 11 Samples for small rivers and deposition

| NERI no. | Sampling date | Site | Position |
|-------------|---------------|-------------|--------------|
| 6.1087 | 96-11-29 | Hove Å | Mouth |
| 6.1088 | 96-11-29 | Hove Å | 5m upstream |
| 6.1089 | 96-11-29 | Maglemose Å | Mouth |
| 6.1090 | 96-11-29 | Maglemose Å | 5 m upstream |
| Start depos | 96-10-30 | | |
| 6.1043-1 | 96-11-13 | Ll.Valby | NW NE |
| 6.1043-2 | 96-11-27 | Ll.Valby | NW NE |
| 6.1203 | 96-12-12 | Ll.Valby | NW NE |
| 7.0014 | 97-01-08 | Ll.Valby | NW NE |
| 7.0053 | 97-02-05 | Ll.Valby | NW NE |
| 7.0141 | 97-03-05 | Ll.Valby | NW NE |
| 7.0198 | 97-04-02 | Ll.Valby | NW NE |
| 7.0518 | 97-04-30 | Ll.Valby | NW NE |

Å = small river Start depos = Start date of first deposition sampling

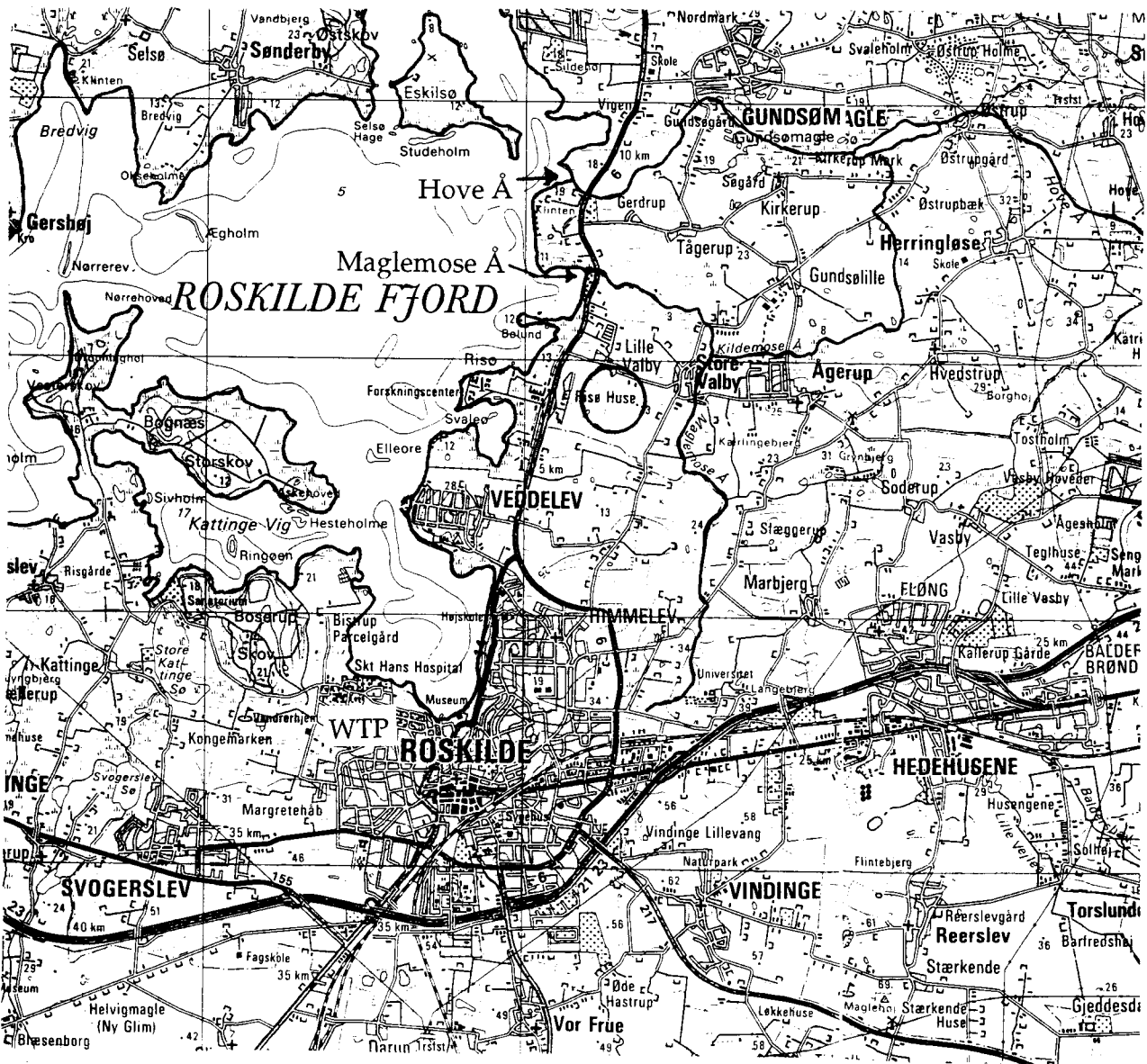


Fig. 4 Map of Roskilde city and surroundings showing the sampling sites (1/100,000)

5 Results and discussion

5.1 Car wash

The results for the car wash site A are summarised in Table 12 and for site B in Table 13. Each table consists of two parts comprising four sections, for identification, concentrations, emission and recovery, respectively.

The results are rounded to two significant digits.

Table 12 Nonylphenoles and phthalates in waste water from car wash site A

| NERI no | 6.1044 | 6.1045 | 6.1046 | 6.1047 | 6.1048 | 6.1049 | 6.1050 |
|-------------------------|--|--------|--------|--------|--------|--------|--------|
| Car manufacturer | H | E | A | E | G | B | K |
| Car building year | 1993 | 1983 | 1994 | 1986 | 1994 | 1995 | 1989 |
| Built in | Europe | Europe | Europe | Europe | Europe | Europe | Japan |
| Analytical method | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| <i>Phthalate</i> | <i>Concentrations in waste water, µg/l</i> | | | | | | |
| NP | 300 | (48) | 530 | 620 | 300 | 200 | 220 |
| NPDE | | | | | | | |
| DBP | | | | | | | |
| DPP | | | | | | | |
| BBP | 26 | 14 | | | 6.6 | | |
| DEHP | 150 | 170 | 130 | (17) | 760 | (5.2) | |
| DnOP | 62 | 11 | 5.8 | 6.2 | 15 | 15 | 9.7 |
| DnNP | | | | 4.2 | 10 | 27 | 5.1 |
| DiNP | na | na | na | na | na | na | na |
| <i>Phthalate</i> | <i>Emissions per single wash, mg</i> | | | | | | |
| NP | 42 | (7) | 75 | 86 | 42 | (28) | 31 |
| NPDE | | | | | | | |
| DBP | | | | | | | |
| DPP | | | | | | | |
| BBP | 4 | 2 | | | 1 | | |
| DEHP | 21 | 24 | 18 | (2) | 110 | (1) | |
| DnOP | 9 | 2 | 1 | 1 | 2 | 2 | 1 |
| DnNP | | | | 1 | 1 | 4 | 1 |
| DiNP | na | na | na | na | na | na | na |
| <i>Extraction spike</i> | <i>Recovery, %</i> | | | | | | |
| D ₄ -DBP | 73 | 73 | 73 | 73 | 73 | 73 | 73 |
| D ₄ -BBP | 53 | 53 | 53 | 53 | 53 | 53 | 53 |
| D ₄ -DEHP | 80 | 80 | 80 | 80 | 80 | 80 | 80 |

Results corrected by the average recovery from method 2, shown in the recovery section, blank subtracted

na = not analysed

Space = not detected

Uncertain results below determination limits in ().

In the last column of each table, the limits of determination are given, rounded to one digit. Un-detected (negative results when blank has been subtracted) are marked as empty spaces in the table, uncertain results below determination limits, shown in parenthesis. The recoveries for method 1 are not analysed, but the results corrected by the average recovery from method 2 (marked in *italics*). The correction by this approach improves the accuracy, since the extraction procedures for methods 1 and 2 are comparable.

The emissions given in mg per single wash are calculated from the concentrations assuming a washing volume of 140 l according to information available from car wash site A.

Table 12 (continued) Nonylphenoles and phthalates in waste water from car wash site A

| NERI no | 6.1051 | 6.1052 | 6.1053 | 6.1054 | 6.1055 | 6.1056 | 6.1080 | Determ |
|-------------------------|--|--------|--------|--------|--------|--------|--------|--------|
| Car manufacturer | C | E | J | E | B | F | F | Limit |
| Car built year | 1993 | 1995 | 1996 | 1994 | 1987 | 1996 | 1996 | |
| Built in | Europe | Europe | Japan | Europe | Europe | Europe | Europe | |
| Analytical method | 1 | 1 | 1 | 1 | 1 | 1 | 2 | |
| <i>Phthalate</i> | <i>Concentrations in waste water, µg/l</i> | | | | | | | |
| NP | | 300 | 660 | (170) | 230 | (66) | | 200 |
| NPDE | | | | | | | (6) | 7 |
| DBP | | 200 | 300 | 430 | 810 | | 110 | 100 |
| DPP | | | | | | | | 0.2 |
| BBP | | | 37 | 110 | 150 | 49 | 3 | 2 |
| DEHP | | 100 | 100 | 170 | 260 | (34) | 89 | 40 |
| DnOP | 4.0 | 12 | 21 | 19 | 16 | 23 | 4 | 0.8 |
| DnNP | | 12 | 28 | 16 | 46 | 24 | 5 | 1 |
| DiNP | na | na | na | na | na | na | 88 | |
| <i>Phthalate</i> | <i>Emissions per single wash, mg</i> | | | | | | | |
| NP | | 41 | 93 | (24) | 32 | (9) | | 30 |
| NPDE | | | | | | | 1 | 1 |
| DBP | | 28 | 41 | 60 | 110 | | 15 | 14 |
| DPP | | | | | | | | 0.03 |
| BBP | | | 5 | 15 | 20 | 7 | | 0.3 |
| DEHP | | 14 | 14 | 23 | 37 | (5) | 12 | 6 |
| DnOP | 1 | 2 | 3 | 3 | 2 | 3 | 1 | 0.1 |
| DnNP | | 2 | 4 | 2 | 6 | 3 | 1 | 0.1 |
| DiNP | na | na | na | na | na | na | 12 | |
| <i>Extraction spike</i> | <i>Recovery, %</i> | | | | | | | |
| D ₄ -DBP | 73 | 73 | 73 | 73 | 73 | 73 | 67 | |
| D ₄ -BBP | 53 | 53 | 53 | 53 | 53 | 53 | 70 | |
| D ₄ -DEHP | 80 | 80 | 80 | 80 | 80 | 80 | 93 | |

Results corrected by the average recovery from method 2, shown in the recovery section, blank subtracted

na = not analysed

Space = not detected.

Uncertain results below determination limits in ()

Table 13 Nonylphenoles and phthalates in waste water from car wash site B

| NERI no | 7.0002 | 7.0003 | 7.0004 | 7.0005 | 7.0006 | 7.0007 | 7.0008 |
|-------------------------|--|--------|--------|--------|--------|--------|--------|
| Car manufacturer | E | L | L | I | F | H | L |
| Car built year | 1996 | 1987 | 1993 | 1987 | 1996 | 1996 | 1993 |
| Built in | Europe | Japan | Japan | Europe | Europe | Europe | Japan |
| Analytical method | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Phthalate | Concentrations in waste water, µg/l | | | | | | |
| NP | | | | | | | |
| NPDE | | | | | | | |
| DBP | | | (33) | | | | |
| DPP | | | | 4 | | | |
| BBP | | 3 | | 10 | (0.5) | | |
| DEHP | 11 | 74 | 76 | 140 | 100 | 53 | 94 |
| DnOP | | 14 | (0.7) | | 15 | 8.4 | 22 |
| DnNP | 2 | 55 | 4.6 | 5.8 | 8.7 | 4.3 | |
| DiNP | | 390 | | | 340 | 430 | 230 |
| Phthalate | Emissions per single wash, mg) | | | | | | |
| NP | | | | | | | |
| NPDE | | | | | | | |
| DBP | | | (5) | | | | |
| DPP | | | | 0.6 | | | |
| BBP | | 0.4 | | 1 | (0.1) | | |
| DEHP | 2 | 10 | 11 | 20 | 14 | 7 | 13 |
| DnOP | | 2 | (0.1) | | 2 | 1 | 3 |
| DnNP | 0.3 | 8 | 0.6 | 0.8 | 1 | 1 | |
| DiNP | | 55 | | | 47 | 60 | 33 |
| Extraction spike | Recovery, % | | | | | | |
| D ₄ -DBP | 99 | 65 | 104 | 54 | 105 | 85 | 64 |
| D ₄ -BBP | 72 | 42 | 77 | 46 | 78 | 66 | 49 |
| D ₄ -DEHP | 85 | 77 | 78 | 63 | 89 | 82 | 68 |

Results corrected for recovery, blank subtracted

Space = not detected. Uncertain results near or below determination limits in ()

Table 13 (continued) Nonylphenoles and phthalates in waste water from car wash site B

| NERI no | 7.0009 | 7.0010 | 7.0011 | 7.0012 | 7.0013 | Limits |
|-------------------------|--|--------|--------|--------|--------|---------|
| Car manufacturer | E | D | C | K | C | of |
| Car built year | 1996 | 1987 | 1994 | 1995 | 1992 | Determ. |
| Built In | Europe | Europe | Europe | Japan | Europe | |
| Analytical method | 2 | 2 | 2 | 2 | 2 | 2 |
| <i>Phthalate</i> | <i>Concentrations in waste water, µg/l</i> | | | | | |
| NP | | | | | | 30 |
| NPDE | | | | | | 6 |
| DBP | (30) | | | | | 60 |
| DPP | | | | | | 0.2 |
| BBP | | (1.2) | | (1.5) | | 2 |
| DEHP | 80 | 67 | 140 | 26 | 67 | 3 |
| DnOP | | 11 | 10 | | 4.0 | 0.6 |
| DnNP | | 3.8 | 7.1 | | 2.6 | 0.9 |
| DiNP | 510 | 430 | 230 | 370 | 480 | 50 |
| <i>Phthalate</i> | <i>Emissions per single wash, mg</i> | | | | | |
| NP | | | | | | 4 |
| NPDE | | | | | | 0.9 |
| DBP | (5) | | | | | 8 |
| DPP | | | | | | 0.03 |
| BBP | | (0.2) | | (0.2) | | 0.3 |
| DEHP | 11 | 9 | 20 | 4 | 9 | 0.5 |
| DnOP | | 2 | 1 | | 1 | 0.1 |
| DnNP | | 0.5 | 1 | | 0.3 | 0.1 |
| DiNP | 71 | 60 | 32 | 52 | 68 | 7 |
| <i>Extraction spike</i> | <i>Recovery, %</i> | | | | | |
| D ₄ -DBP | 61 | 77 | 74 | 59 | 106 | |
| D ₄ -BBP | 57 | 47 | 47 | 43 | 66 | |
| D ₄ -DEHP | 69 | 72 | 77 | 79 | 95 | |

Results corrected for recovery, blank subtracted

Space = not detected. Uncertain results below determination limits in ()

As can be seen from Table 12 and Table 13, a single car wash gives off nonylphenoles as well as phthalates in milligram amounts, and this emission varies much between the individual washing tests. The question arises whether there is a difference between site A with the reverse osmosis and site B with the conventional water system, between Japanese and European cars, and between the type of wash.

Selected averages

In Table 14 selected averages of the results are summarised. In the upper part of the table, the average concentrations of nonylphenoles and phthalates in the waste water are given, together with the average and the standard deviation for the total. In the lower part of the table, the emissions in mg per wash are given.

Table 14 Average concentrations and emissions of nonylphenoles and phthalates from car wash

| | n | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP |
|--|----|-----|------|-----|------|-----|------|------|------|------|
| <i>Average concentrations in waste water, µg/l</i> | | | | | | | | | | |
| Site A | 14 | 260 | 0.4 | 131 | | 28 | 142 | 16 | 13 | na |
| Site B | 12 | | | 5 | 0.3 | 1 | 78 | 7 | 8 | 284 |
| European | 20 | 138 | 0.3 | 79 | 0.2 | 18 | 127 | 12 | 9 | 278 |
| Japanese | 6 | 147 | | 54 | | 7 | 62 | 11 | 16 | 250 |
| With undercar rinse | 3 | | | | | | 72 | 11 | 2 | 382 |
| Without undercar rinse | 23 | 159 | 0.3 | 83 | 0.2 | 18 | 117 | 12 | 11 | 235 |
| Total | 26 | 140 | 0.2 | 73 | 0.1 | 16 | 112 | 12 | 10 | 269 |
| Standard deviation | 26 | 204 | 1.2 | 183 | 0.7 | 35 | 146 | 13 | 14 | 191 |
| <i>Average emission per wash, mg</i> | | | | | | | | | | |
| Site A | 14 | 36 | 0.06 | 18 | | 3.9 | 20 | 2.2 | 1.8 | na |
| Site B | 12 | | | 1 | 0.04 | 0.2 | 11 | 1.0 | 1.1 | 40 |
| European | 20 | 19 | 0.04 | 11 | 0.03 | 2.5 | 18 | 1.7 | 1.2 | 39 |
| Japanese | 6 | 21 | 0.00 | 8 | | 1.0 | 9 | 1.6 | 2.2 | 35 |
| With undercar rinse | 3 | | | | | | 10 | 1.6 | 0.3 | 54 |
| Without undercar rinse | 23 | 22 | 0.04 | 12 | 0.02 | 2.5 | 16 | 1.7 | 1.6 | 33 |
| Total | 26 | 20 | 0.03 | 10 | 0.02 | 2.2 | 16 | 1.7 | 1.5 | 38 |
| Standard deviation | 26 | 29 | 0.16 | 26 | 0.10 | 5.0 | 20 | 1.8 | 2.0 | 27 |

Standard deviation of total in same units as averages.

As can be seen from the total-rows of the table, the most significant phthalates are DBP, DEHP and DiNP.

Comparing the concentrations in Table 14 with the concentrations for the waste water treatment plant (described in section 5.4), about doubled concentrations for DEHP and DiNP are shown. Thus the car wash must contribute these phthalates to the waste water.

The high blank of the BBP measurements, however, leads to many un-detects. DiNP was not measured from site A, and is furthermore close to detection limit in spite of a rather high concentration, because it is distributed on many single-substances in low concentrations. Therefore these results are unsuited for comparisons. Hence, to make valid statistical testing, DEHP is addressed in the following.

Statistical tests

As can be seen, the average DEHP concentration at site A is higher than at site B. Since the variances differ significantly ($F=24$, $p=0.003$), a t-test for unequal variances must be performed. By this test no significant difference was found between sites ($p=0.12$). By a Wilcoxon-test no significant difference was found either ($p<0.1$). In conclusion, there is no significant difference between the average DEHP-concentrations at the two sites.

In the same way, the difference between DEHP concentrations for Japanese and European cars can be tested and in this case the difference is weakly significant by the t-test (unequal variances, $p = 0.06$). By the Wilcoxon test no significant difference was found ($p = 0.1$), but this test is less sensitive than the t-test. In conclusion,

these tests indicate that the European cars do give off more DEHP than the Japanese.

Another question is whether an influence of the washing program can be seen. It could be expected that the undercar-rinse enhances the washing out of the phthalates from the undercar rust protection, leading to increased emission. Unfortunately, only three washes without undercar rinse occurred during the whole experimental session. No significant difference was found (t-test unequal variances, $p=0.3$).

Influence of age

Another interesting aspect is whether an influence of the age of the cars is discernible in the data. This is illustrated for European cars in Fig. 5 and for Japanese in Fig. 6, which show the concentrations of four selected phthalates in the washing water, sorted according to the building year of the cars. To facilitate comparison, the figures are drawn to same vertical scale.

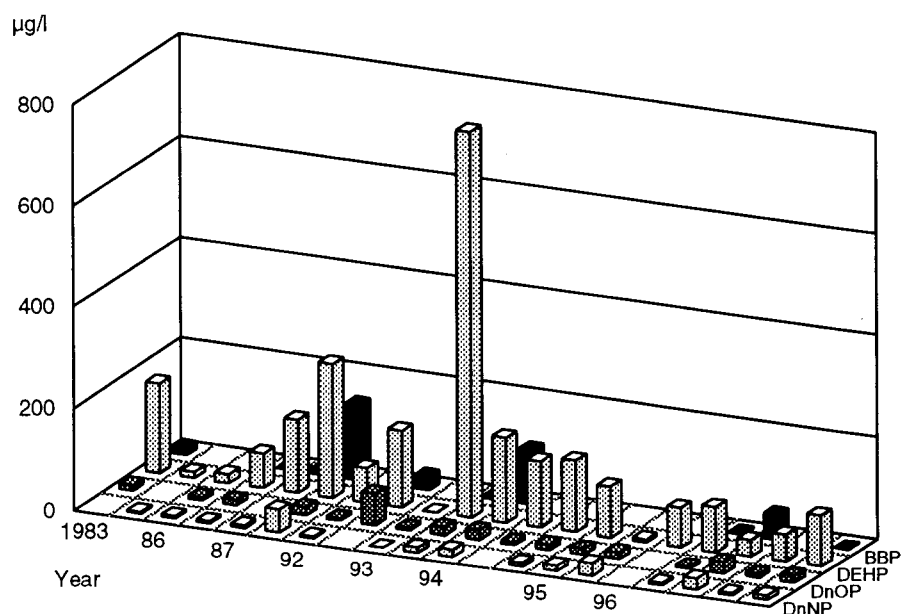


Fig. 5 Concentrations of the four most abundant phthalates in washing water from European cars, sorted according to building year of cars.

In both figures, DEHP appear to be the phthalate occurring in the highest concentration. In Fig. 5, there is a large scatter of the DEHP concentrations, but there seems to be a maximum in the middle of the year-span.

Other things being equal, it should be expected that the older the car, the more phthalates had been washed out, thus leading to a decrease of DEHP concentration with age (a "washing-out signature"). However, such a pattern is not visible.

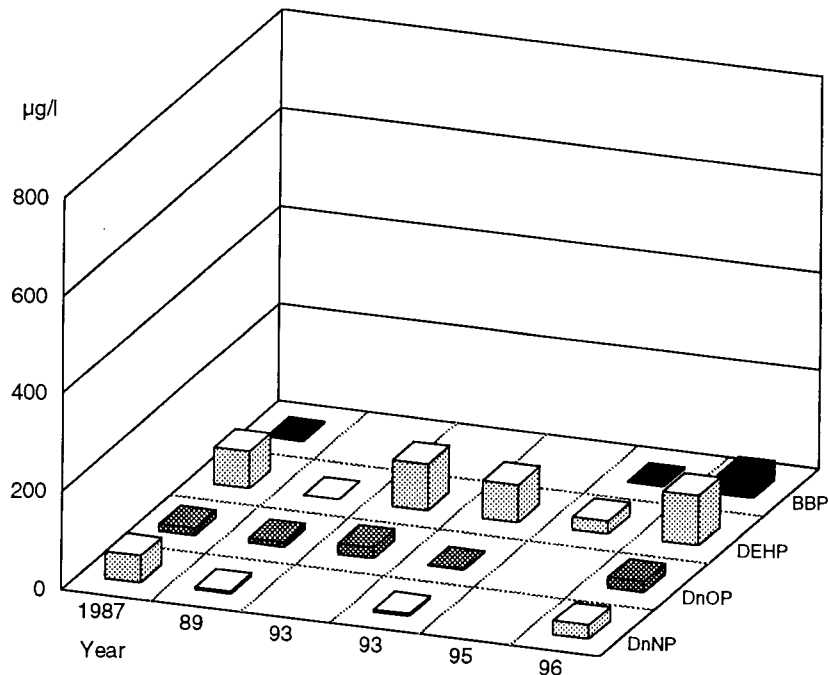


Fig. 6 Phthalate concentrations in water from washing of Japanese cars, sorted according to building year (same vertical scale as Fig. 5).

This may be due to decreasing amounts of DEHP used in the manufacture of cars over the years, which would suppress the washing-out signature by lowering the concentration from newer cars. An alternative explanation could be that some of the old cars recently were treated with lacquer or corrosion protectives containing DEHP, which would mask the washing-out signature by increasing the concentration from old cars. Finally, the washing out signature may simply be too weak to be seen in the scatter of data from different car models.

It is clearly seen that the Japanese cars shown in Fig 6. generally display a somewhat lower DEHP concentration in a narrower range, compared to the European. This is in agreement with the statistical test mentioned above. No age-effect can be seen on Japanese cars, but this might be due to the more sparse data set.

Annual emissions

In the lower part of Table 14, it is seen that the total average emissions per wash of DEHP and DiNP are estimated to 16 and 38 mg, respectively.

To calculate the emission per year from each plant, the number of car washes must be known. According to information from site A, 17000 car washes per year are carried out. Multiplying this number with the emission per wash yields the total annual emission for that plant, given in Table 15. For the other plant with conventional washing system, however, this information was not available. Nevertheless it is possible to estimate the annual emission for that plant by utilising information about the water consumption supplied by the municipal water works. For site A with a known

number of washes, the car washing consumes $17000 * 0.14 \text{ m}^3 = 2380 \text{ m}^3$ per year. The water supplied annually amounts to 3010 m^3 (average of 2 years) according to the water works. The car wash thus consumes 79% of the total water consumption of the plant. The annual water consumption for plant B is 2953 m^3 , and assuming that the car wash consumes 80%, this amounts to 2362 m^3 . The annual emission from that plant can then be calculated from the average concentrations. These results are given in Table 15, together with the average per plant and the estimated annual water consumption for car washing.

The annual national emission can be estimated from the number of cars (1,744,337 at January 1996), an assumed 26 washes per car per year, and the total average emission per wash from Table 14. These results are given in Table 15 in kg/y.

Table 15 Estimated annual emissions for car wash

| | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | Water |
|---------------|---------------------------------------|------|-----|-----|-----|------|------|------|------|------------------------|
| | <i>Annual emission per plant, g/y</i> | | | | | | | | | <i>m³/y</i> |
| Site A | 620 | 1.0 | 313 | 0 | 66 | 337 | 38 | 30 | na | 2380 |
| Site B | | | 13 | 0.7 | 3 | 183 | 17 | 19 | 672 | 2362 |
| Plant average | 310 | 0.5 | 163 | 0.4 | 35 | 260 | 27 | 24 | 672 | 2371 |
| | <i>Annual emission, kg/y</i> | | | | | | | | | |
| National | 891 | 1.4 | 465 | 0.9 | 99 | 712 | 75 | 66 | 1710 | |

As can be seen, plant A using the reverse osmosis system seems to have a somewhat higher emission of DEHP, perhaps contrary to expectations. However, the data should not be over-interpreted, since the two types of plants are measured with slightly different methods. The water consumptions for the two plants are comparable. The estimated total emission for the eight car washing plants in Roskilde amounts to a few kg/y for DEHP, assuming that the annual emission from each plant is close to the plant average in Table 15. The total Danish national annual emission is estimated to 712 kg/y DEHP and 1710 kg/y DiNP.

Discussion

Since the car wash samples were taken in the washing room and not at the outlet discharge, they may not be fully representative for the emission into the municipal sewer system. As described in the samples section, a waste water outlet train is installed at the car wash stations comprising sand trap, reservoir and oil trap. The function of the sand trap is to collect sand and other heavy particles, and the oil trap to collect oil. In the reservoir, located between the sandtrap and the oil trap, waste water to be used for undercar rinse is stored. A question is whether the phthalates to some extent are removed by the passage through the train. According to a recent investigation (Miljøstyrelsen 1997b) significant amounts of phthalates, especially DEHP, were found in sediment in the sand trap of a storm water system. However, the car wash waste water has much higher concentrations of detergents, tending to emul-

gate the phthalates. Hence, they will presumably not precipitate significantly in the traps. Phthalates may also be adsorbed on the internal surfaces on the system, but due to the continued exposure to phthalates, the surfaces will gradually become saturated, whereby steady state concentration conditions eventually will be reached. If these assumptions are correct, the concentrations will not be altered much by the passage through the different compartments of the waste water train to the outlet discharge. Of course, the above arguments apply to the municipal sewer system also, which has much larger internal surfaces.

Another mechanism may be dissolution of phthalates in the oil layer of the oil trap or accumulation in the oil-water or air-water interface (Aveyard e.a. 1994). This problem has not been addressed in the present investigation, and it is not known whether an oil layer is present.

5.2 Institutions and industry

Hospital & laundry

The results for the hospital and the industrial laundry are compiled in Table 16.

Since results are analysed by the same method (method 2), in the same dilution (1/100), they have the same limit of determination, shown in the table.

Table 16 Nonylphenoles and phthalates in waste water from hospital and laundry

| NERI no. | 6.1069 | 6.1070 | 6.1071 | 6.1072 | 6.1073 | 6.1074 | 6.1009 | 6.1010 | Limit |
|-------------------------|--|--------|----------------|--------|------------|--------|---------|--------|--------|
| Site | Hospital | | | | | | Laundry | | of |
| Position | Parking | | X-ray building | | Physicians | | | | Determ |
| <i>Phthalate</i> | <i>Concentrations in waste water, µg/l</i> | | | | | | | | |
| NP | | (2.4) | | | | | | | 30 |
| NPDE | | | | (3.4) | | | | | 6 |
| DBP | 118 | 102 | | | | | | | 60 |
| DPP | | | 0.3 | 0.6 | (0.1) | 0.6 | | | 0.2 |
| BBP | (0.2) | (0.3) | | | | | | | 2 |
| DEHP | 7.3 | 35 | 11 | 20 | 16 | (2.1) | 91 | 130 | 3 |
| DnOP | | 2.5 | | | | | 4.8 | 4.6 | 0.6 |
| DnNP | | 2.1 | 1.5 | (0.7) | | | | 8.3 | 0.9 |
| DiNP | | | | | | | | | 50 |
| <i>Extraction spike</i> | <i>Recovery, %</i> | | | | | | | | |
| D ₄ -DBP | 74 | 33 | 76 | 57 | 76 | 81 | 102 | 116 | |
| D ₄ -BBP | 53 | 27 | 62 | 50 | 65 | 63 | 78 | 86 | |
| D ₄ -DEHP | 101 | 40 | 72 | 53 | 73 | 83 | 86 | 90 | |

Space = not detected, limits of determination given in the last column.

The blank (average of 5) has been subtracted from the results.

Uncertain results below determination limit in ()

As can be seen for the hospital results, there seems to be some DBP at the parking lot, and some DPP at the physicians building, but all these phthalates are close to the limit of determination. DEHP is the phthalate occurring in the highest concentration and seems to be rather evenly distributed between the three sites, even if the scatter of values is large. There is thus no indication of a larger concentration near the x-ray building compared to the other sites.

The concentration of DEHP is below the inlet concentration of the waste water treatment plant (WTP) described in Section 5.4.

The laundry has a significantly higher concentration of DEHP than the hospital. Contrary to expectations no NP or NPDE was detected. The concentration of DEHP is above the inlet concentration of the WTP.

Kindergarten & adhesives

The results for the kindergarten and the adhesives industry are shown in Table 17, all analysed by method 2. These samples had a very high concentrations making a dilution of 1/10000 necessary to avoid saturation of the MS signal. The results have a common limit of determination shown in the table. Unfortunately, the concentrations of extraction spikes in the very dilute samples were too low to be detected. Hence, the recovery for these spikes cannot be given. Furthermore, it was not possible to calculate the results as normal for method 2 using the extraction spikes. Instead they are calculated in the same way as in method 1 using the syringe spike as a basis.

Table 17 Concentrations of nonylphenoles and phthalates from adhesives industry and kindergarten

| NERI no. | 6.1067 | 6.1007 | 6.1008 | Limit |
|-----------|-------------------------------------|-----------|--------|--------|
| Site | Kinderg | Adhesives | | of |
| Situation | Normal | Spill | Normal | Determ |
| Phthalate | Concentrations in waste water, ug/l | | | |
| NP | (1600) | (1000) | (1600) | 3000 |
| NPDE | 11000 | (31) | (27) | 500 |
| DBP | | | 86000 | 1000 |
| DPP | 130 | 94 | (40) | 40 |
| BBP | 320 | 210 | 1400 | 40 |
| DEHP | | | | 600 |
| DnOP | 310 | 280 | | 60 |
| DnNP | 280 | | | 80 |
| DiNP | | (7500) | (8400) | 20000 |

Space = not detected

The blank of corresponding dilution has been subtracted from the results. Uncertain results near or below determination limits in ()

As can be seen, a significant concentration of NPDE is present in the waste water from the kindergarten, which is the only site in

the investigation where this is the case. Also, there seems to be detectable amounts of the otherwise rarely occurring DPP and BBP. This high concentration for the kindergarten was not expected, hence only two samples were planned, one of which was lost due to breakage of the bottle during freezing.

With only a single sample analysed, the results are not representative and must be regarded as uncertain.

The use of materials in the kindergarten was investigated by interrogating the leader and employees about the make and amount of paints and waxes used. The exact amount used per day was unknown. It was attempted to get information about the content of nonylphenoles and phthalates from the general database of product of the ministry of environments, but these data were not present.

Another possibility might be emission of phthalates due to the washing of vinyl floors (Vikelsøe 1995). However, as remarked in the samples section, only a small floor area in the lavatories were covered by this material, the other floors being covered with linoleum.

For the adhesives industry, an extremely large concentration of DBP is seen in the "normal operation" sample, whereas DBP for the "spilling episode" samples is below determination limit. This is very surprising since the reverse was expected. A possible explanation for this could be a time delay before the water reaches the sewer well, which is located outside the building. Since the spilling episode was sampled first, the water from this may have arrived later, during the sampling called the normal operation. Neither for kindergarten or adhesives industry, DEHP is detected.

The results for institutions and industry are summarised in Table 18. The annual emissions are calculated from the annual water consumption (1996) according to the municipal water works, stated in the last column. For the adhesives industry, the figures for the least concentrated sample are used for the concentrations, rather than the average.

Table 18 Average concentrations and annual emissions for institutions and industry

| | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | Water |
|--------------|--|-------|------|-----|-----|------|------|------|------|---------------------------------|
| | <i>Average concentrations in waste water, µg/l</i> | | | | | | | | | |
| Hospital | 0.4 | 0.6 | 36.6 | 0.3 | 0.1 | 15 | 0.4 | 0.7 | | |
| Kindergarten | 1637 | 10832 | | 131 | 315 | | 311 | 277 | 399 | |
| Laundry | | | | | | 111 | 4.7 | 4.2 | | |
| Adhesives | 1003 | 31 | | 94 | 209 | | 277 | | 7515 | |
| | <i>Average annual emissions, g/y</i> | | | | | | | | | |
| Hospital | 30 | 42 | 2714 | 20 | 6 | 1135 | 31 | 53 | | <i>m³/y</i> 74142 |
| Kindergarten | 1491 | 9868 | | 120 | 287 | | 283 | 252 | 363 | 911 |
| Laundry | | | | | | 3650 | 154 | 137 | | 32903 |

As can be seen, a very high NPDE concentration is found in the outlet from the kindergarten, and a high DiNP concentration in the outlet from the adhesive industry. The kindergarten displays the highest annual emission of NP and NPDE, whereas the hospital and laundry emit the highest amounts of DEHP. It must be stressed again that the kindergarten result relies on *only one* sample, hence it is very uncertain whether this result is representative for kindergartens in general. The annual emission from the adhesives industry is not calculated because of the location in another town, hence it is not relevant for the emission budget in Roskilde.

5.3 Deposition and small rivers

The results from the deposition are shown in Table 19.

Note that the concentrations are given in $\mu\text{g}/\text{m}^3$.

The temperatures given are mean temperatures in each sampling period, calculated from the temperatures measured with 30 min intervals at Lille Valby meteorological station (Risø 1997).

The annual depositions in $\mu\text{g}/\text{m}^2$ (the deposition rates) are calculated from an area of the sampling funnels of 300 cm^2 and the sampling duration in weeks given in the table from *each sample*. In one case snow was present in the samples, marked with *.

As can be seen, DEHP and DBP are most abundant, followed by BBP and DnOP. The concentration values given in the table, which are calculated from the bulk deposition divided by the volume of water, are not identical with the actual concentration in the wet deposition, which has not been measured. Preliminary experiments showed that a part of the phthalates in the sampler are located on the funnel, indicating that the true concentration in the wet deposition is lower. However, these concentrations are given for comparison with the other concentrations in the project.

The deposition rate of DEHP ranges from 140 to $540\ \mu\text{g}/\text{m}^2/\text{y}$, in good agreement with recent studies (Miljøstyrelsen 1996b), which found $140\text{-}1000\ \mu\text{g}/\text{m}^2/\text{y}$.

Table 19 Deposition of nonylphenoles and phthalates at Lille Valby meteorological station

| DMU no | 6.1043 1 | 6.1043 2 | 6.1203 | 7.0014 | 7.0053 | 7.0141 | 7.0198 | 7.0518 | Limit |
|-------------------------|--|----------|--------|--------|--------|--------|--------|--------|-------|
| Year | 1996 | | | 1997 | | | | | of |
| Week no | 46 | 48 | 50 | 2 | 6 | 10 | 14 | 18 | Deter |
| Period, weeks | 2 | 2 | 2 | 4 | 4 | 4 | 4 | 4 | |
| Deposition ml | 1400 | 600 | 750 | * 300 | 250 | 1000 | 350 | 800 | |
| Depos mm/y | 1213 | 520 | 650 | 130 | 108 | 433 | 152 | 347 | |
| Mean temp °C | 8.57 | 3.43 | 2.46 | -3.30 | -0.26 | 4.01 | 5.05 | 4.41 | |
| Phthalate | Concentration, µg/m³ | | | | | | | | |
| NP | 80 | | | | | | | (11) | 25 |
| NPDE | | | | | | | | | 150 |
| DBP | 250 | 590 | 290 | 780 | 1100 | 110 | 290 | 130 | 20 |
| DPP | | | | | | | | | 4 |
| BBP | 33 | 62 | 49 | 130 | | 22 | 120 | 78 | 0.3 |
| DEHP | 450 | 510 | 420 | 1600 | 1300 | 270 | 1000 | 470 | 90 |
| DnOP | (7) | 120 | 110 | 170 | | 79 | 38 | 43 | 10 |
| DnNP | | | | | | | | | 20 |
| DiNP | | | | | | | | | 100 |
| Phthalate | Deposition rate, µg/m²/y | | | | | | | | |
| NP | 95 | | | | | | | (4) | 9 |
| NPDE | | | | | | | | | 50 |
| DBP | 300 | 310 | 190 | 100 | 110 | 49 | 44 | 46 | 8 |
| DPP | | | | | | | | | 1 |
| BBP | 41 | 32 | 32 | 17 | | 10 | 18 | 27 | 0.1 |
| DEHP | 540 | 260 | 280 | 210 | 140 | 120 | 150 | 160 | 30 |
| DnOP | 9 | 62 | 71 | 22 | | 34 | 6 | 15 | 4 |
| DnNP | | | | | | | | | 7 |
| DiNP | | | | | | | | | 40 |
| Extraction spike | Recovery, % | | | | | | | | |
| D ₄ -DBP | 125 | 107 | 132 | 139 | 115 | 135 | 140 | 141 | |
| D ₄ -BBP | 115 | 114 | 106 | 127 | 110 | 116 | 117 | 116 | |
| D ₄ -DEHP | 98 | 84 | 87 | 92 | 91 | 83 | 107 | 106 | |

Space = not detected

Results corrected for recovery, blank subtracted

* snow

Uncertain results below determination limit in ()

Seasonal variation

The seasonal influence on the deposition of DEHP is illustrated in Fig. 7. The back row in the bar graph shows the annual wet deposition calculated from the amount of water in *each sampling bottle*, given in mm/year. In the middle rows the concentrations and the deposition rate (the annual depositions per m²) are shown, and in the front row the temperature (scaled and shifted to accommodate the figure). The deposition rate compensates for the different lengths of the sampling periods.

It is seen that the deposition rate of DEHP is highest in the fall of 1996 (week no. 46), and decreases smoothly until in week no. 10 1997 a minimum is reached. It then starts to rise again during the spring. In contrast, the concentration values appear more erratic, having a large random variation, as is also the case for the wet deposition.

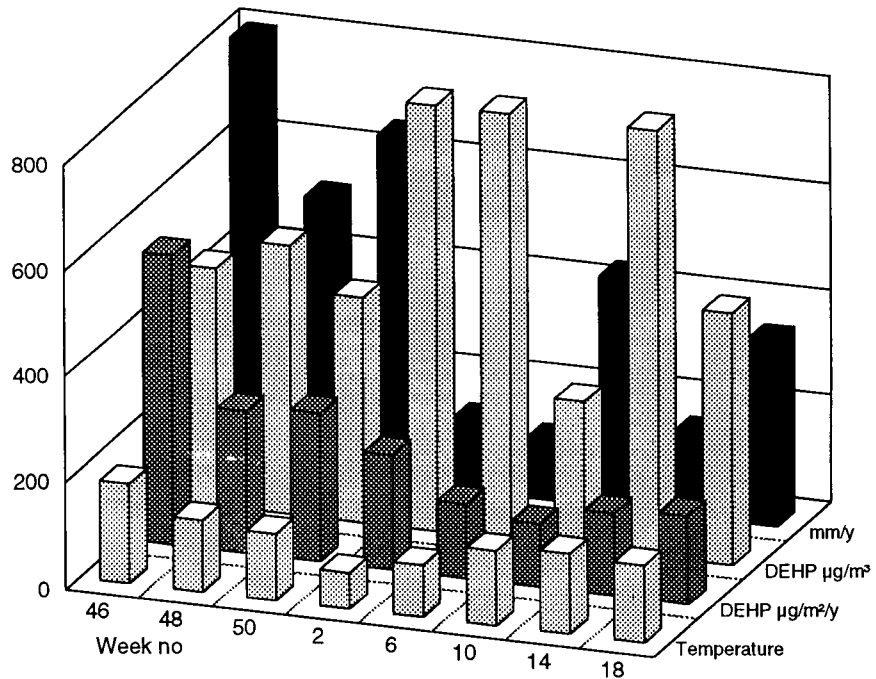


Fig. 7 Seasonal variation of wet deposition, deposition of DEHP and temperature (scaled to fit the graph), winter 1996 to 1997.

These findings indicate that the deposition of DEHP is comparatively independent of the wet deposition, reflecting the role of dry deposition. Hence, the deposition rate appear to be a more realistic measure, shown in Fig. 8 for the four most abundant phthalates.

As can be seen in Fig. 8, the minimum is more pronounced for DBP than for DEHP, being deeper and longer.

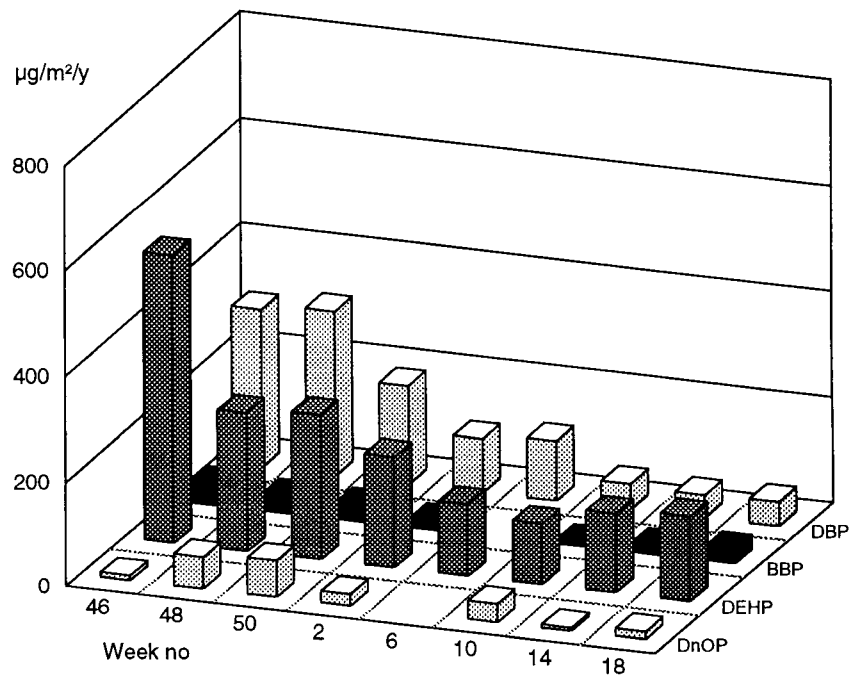


Fig. 8 Seasonal variation of deposition rates (annual deposition per m²) of the four phthalates occurring in the highest concentrations.

Also for BBP and DnOP a minimum is seen, but it appears somewhat weaker, probably due to the lower values of these substances near the analytical determination limits.

Discussion

There could be several reasons for the observed minimum. First it could be due to a pure temperature effect, which would reduce the evaporation from the sources in the winter, thus lowering the air concentrations, which in turn would lead to reduced deposition. From Fig. 7 it is seen that the mean temperature follows a similar trend, but that the temperature minimum occurs in week 2. The deposition minimum thus occurs about 8 weeks after the temperature minimum. A delay must be expected since it will take some time for the atmosphere to respond to the emission changes brought about by the changes in temperature. This is especially true if the sources are evenly distributed geographically over a large area, as indicated by the wind studies mentioned below. Shifting the temperature data 8 weeks so the minimum corresponds with the DEHP minimum, a highly significant correlation is found ($r = 0.88$, $n = 6$, $p < 0.01$).

Another possibility might be seasonal variation in the outdoor use of materials containing phthalates. For example, DBP is contained in sealants used in building construction and maintenance, activities that take place mainly in the summer. This agrees with the stronger minimum of DBP, assuming that the added effects of temperature and use are observed.

A third influential factor could be seasonal variations of the dust concentrations in the air. The results indicate, as previously noted, that the dry deposition may play a significant role in the bulk deposition, very probably mediated by dust. Thus it has been shown that the concentration of DEHP is correlated with the amount of dust particles in the air (Thomsen & Carlsen 1997). The dust concentrations *per se* have not been measured in the present project, however.

Wind speed and direction

A fourth possible factor which might influence the deposition is temporal variations in the wind speed and direction. The wind will affect the amount carried into the area by as well short-range as long-range transport, which may play a significant role according to studies of other environmental pollutants such as organochlorines (Olsson et al. 1997, Schlabach et al. 1997). During the sampling of deposition, the wind speed and direction has been logged on Lille Valby meteorological station every 30 min (Risø 1997). In Fig. 9 these data are shown as rosette diagrams for each sample. The wind intensities from eight directional sectors are plotted, the first sector being 0-45 ° (N-NE) the second 45°-90° (NE-E) etc. The average wind intensities in each sector is calculated by multiplication of wind speed and time summed over the sampling period. This result has dimension of a length, *the wind length*, shown in the figure in units of 1000 km for each sector.

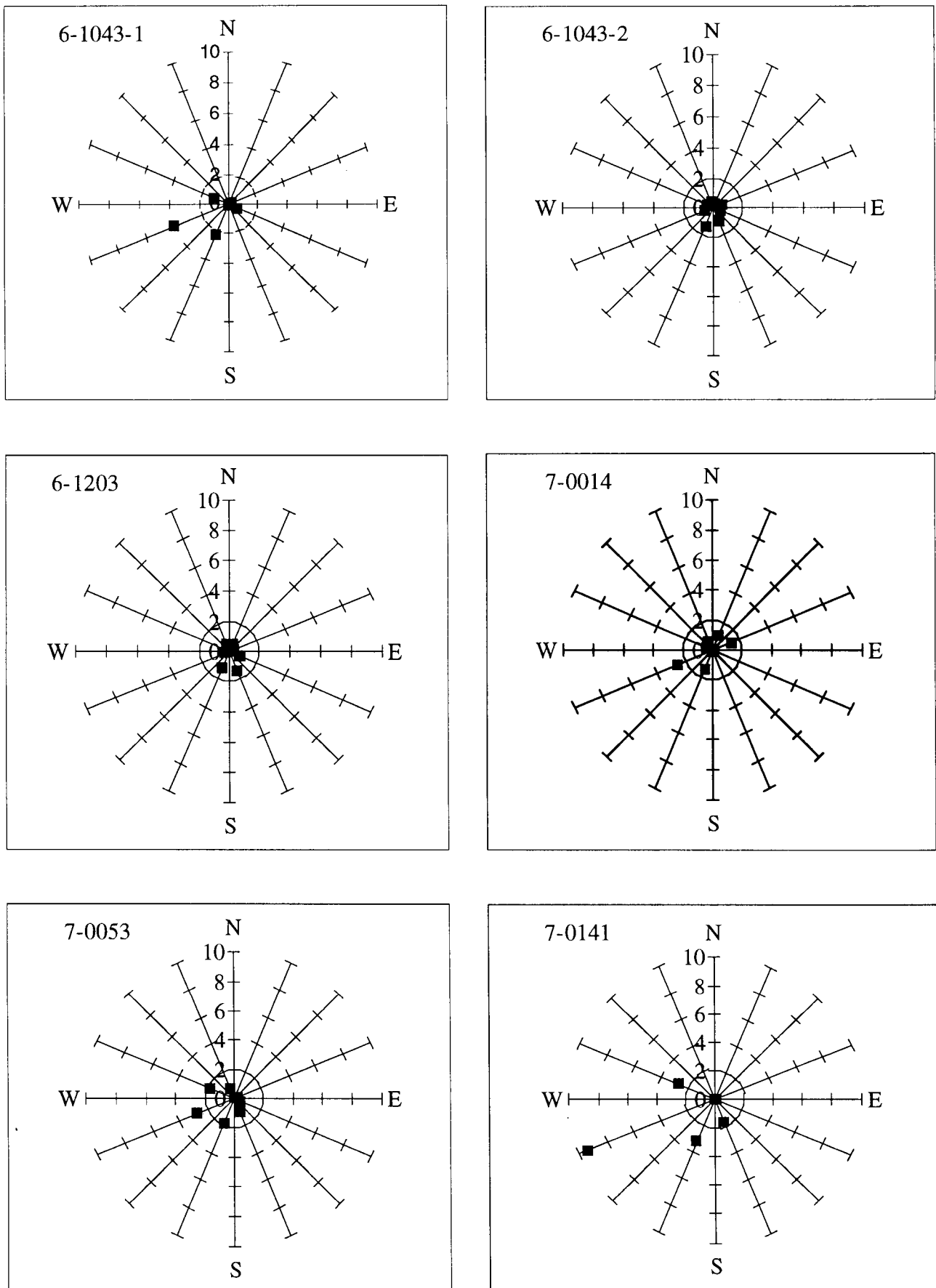


Fig. 9 Wind intensity diagrams for deposition samples. Wind lengths in units of 1000 km, shown as distance from the origin. Radius corresponds to 10,000 km (= distance from Northpole to Equator)

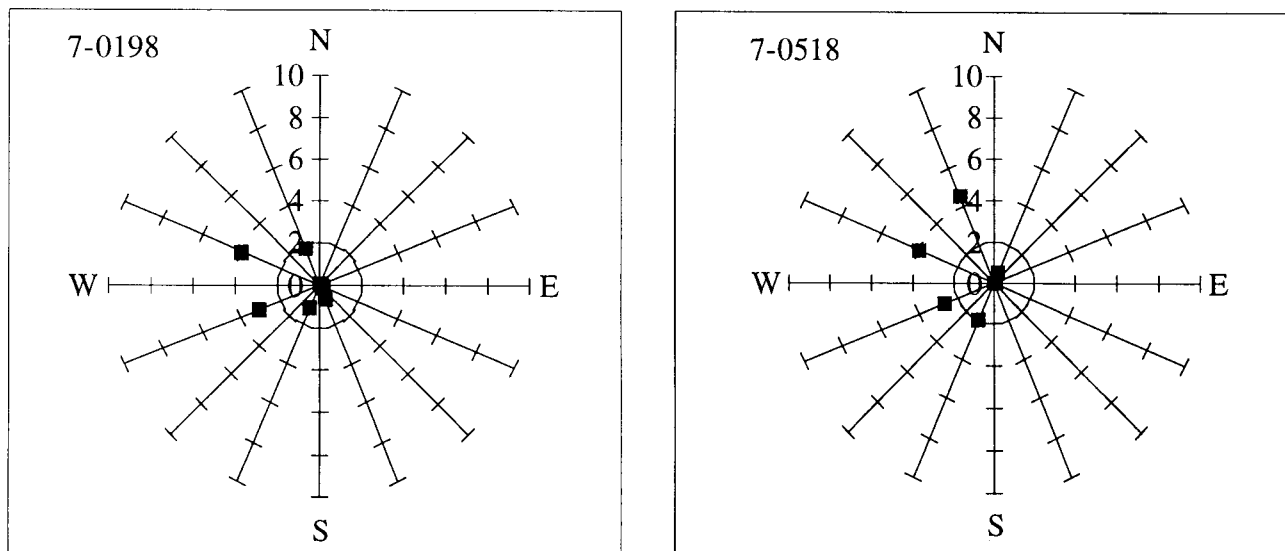


Fig. 9 (continued) Wind intensity diagrams for deposition samples. Wind lengths in units of 1000 km.

As can be seen from the figure, the wind direction has been predominant in the SW sector for the first 6 samples, with great differences in wind length. Especially sample 7.0141 has the record high wind length of almost 10.000 km from WSW, but has the lowest BBP and DEHP deposition rate, whereas the previous sample 7.0053 has much lesser wind but slightly larger deposition rate. Given the same wind direction, the wind length does thus not seem to influence deposition rates. The influence of wind direction can be seen from the last two samples with more northern wind, and especially the last with NW wind. These samples, however, have slightly larger deposition rates than the two previous ones, thus an influence of wind direction is not indicated. This is in contrast to studies of other environmental pollutants such as PCB and PCDD/F (Cleemann et al. 1995, Olsson et al. 1997, Schlabach et al. 1997).

These findings do not exclude the role of long range transport, since the data are too sparse to draw that conclusion. For example, prolonged periods with southern wind blowing from the heavy industrialised central Europe are missing. Furthermore, the data can be explained by long-range transport if ubiquitous sources are evenly geographically distributed over a large part of the Earth.

Small rivers

The results for the small rivers are shown in Table 20. The limits of determination are the same as for the deposition concentrations.

As can be seen, the concentrations in the small rivers are very low, the phthalates occurring in highest concentrations being BBP, DEHP and DnOP. There is a difference between the two rivers, since the concentrations of BBP and DEHP in Hove Å are lower than in Maglemose Å. The concentrations in the river mouths seem to be higher than 5m upstream, especially for Maglemose Å.

Table 20 Nonylphenoles and phthalates in small rivers

| NERI No | 6.1087 | 6.1088 | 6.1089 | 6.1090 | Tapw | Limit |
|----------------------|--|--------|-------------|--------|-------|--------|
| Site | Hove Å | | Maglemose Å | | NERI | of |
| Position | Mouth | 5m ups | Mouth | 5m ups | Lab | Determ |
| Volume, ml | 1400 | 1300 | 1300 | 1250 | 800 | |
| <i>Phthalate</i> | <i>Concentration, µg/m³</i> | | | | | |
| NP | | | | | 830 | 25 |
| NPDE | | | | | | 150 |
| DBP | | | 100 | | 160 | 20 |
| DPP | | (3) | 15 | | | 4 |
| BBP | 29 | 83 | 130 | 160 | 460 | 0.3 |
| DEHP | 140 | 120 | 730 | 190 | 11000 | 90 |
| DnOP | 47 | 54 | 36 | | | 10 |
| DnNP | (22) | | 68 | | | 20 |
| DiNP | | | | | | 100 |
| <i>Extract.spike</i> | <i>Recovery %</i> | | | | | |
| D ₄ -DBP | 142 | 149 | 127 | 142 | 137 | |
| D ₄ -BBP | 112 | 116 | 122 | 104 | 145 | |
| D ₄ -DEHP | 84 | 89 | 108 | 93 | 105 | |

Results corrected for recovery, blank subtracted. Space = not detected.

ups = upstream. Uncertain results near or below determination limit in ()

Tapwater

A water sample from a tap in the laboratory has been analysed for comparison. The DEHP-concentration in the tapwater is almost 40 times higher than the average in the rivers.

Averages & mass flows

In Table 21 the average concentrations, deposition rate and mass flows for deposition and small rivers are compiled. The average for the deposition are weighted by the period length. The annual mass flow which the deposition carries into the sewer system, is estimated from the deposition rate, assuming a target area of 16 km² which corresponds roughly to the urban area of the city (map in Fig. 4, Section 4).

The weighted average of the wet deposition is 363 mm/y, somewhat lower than the average Danish annual deposition of 700 mm, as expected due to the lower deposition during the winter months. Multiplying this figure with the urban area of 16 km² yields the annual deposition volume of water, 5813333 m³/y. The annual mass flow can also be calculated multiplying this volume by the average concentration, but give a slightly different result because of the weighting by volume (instead of time).

The annual mass of nonylphenoles and phthalates which the small rivers carry into Roskilde Fjord are calculated from a flow of 21 l/s for Maglemose Å and 84 l/s for Hove Å (average for 1996 according to official tables from Roskilde Amt authorities).

Table 21 Average concentrations and mass flow for deposition and small rivers

| Site | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | Water |
|-------------|--|------|------|-----|-----|------|------|------|------|------------------------|
| | <i>Average concentration, µg/m³</i> | | | | | | | | | |
| Deposition | 7 | | 268 | | 38 | 465 | 43 | | | |
| Hove Å | | | | 1 | 56 | 130 | 51 | 11 | | |
| Maglemose Å | | | 50 | 7 | 145 | 460 | 18 | 34 | | |
| | <i>Average deposition rate, µg/m²/y</i> | | | | | | | | | |
| Deposition | 8 | | 115 | | 19 | 204 | 23 | | | |
| | <i>Annual mass flow, g/y</i> | | | | | | | | | |
| Deposition | 127 | | 1846 | | 307 | 3268 | 363 | | | <i>m³/y</i> |
| Hove Å | | | | 4 | 149 | 344 | 134 | 29 | | 5813333 |
| Maglemose Å | | | 33 | 5 | 96 | 305 | 12 | 23 | | 2650765 |
| | | | | | | | | | | 662691 |

As can be seen, Hove Å has a lower DEHP concentration average than Maglemose Å, which has almost the same concentration as the deposition. Another remarkable results is the substantially higher concentration of DBP in the deposition. In the lower part of the table showing the annual mass flows it is seen that Hove Å has the highest water flow, making the mass flow of phthalates for the two rivers almost identical. It is noted that the mass flows of DEHP in the rivers are about 10 times smaller than the deposition for the Roskilde urban area (16 km²).

Discussion

A possible cause for the higher concentrations found in the river mouths might be sediment from the fjord being suspended by turbulence. The sediments contain phthalates in large amounts according to findings in another part of the project, studying the fjord. The sediments near the rivers have not been measured, however. Possibly, the high DEHP concentration measured in the mouth of Maglemose Å is an outlier, perhaps caused by the accidental contamination of the sample with fjord sediment. Another possibility might be a higher concentration in the water of the fjord, but this does not explain the difference between the mouths of the two rivers assuming a reasonably constant concentration in the fjord water. This is being measured in the fjord study.

The difference measured between the two rivers may not be statistically significant on a longer time scale since the flow as well as the concentrations in the rivers certainly show seasonal variations. Furthermore, the difference in averages depends on the high result for the mouth of Maglemose Å which as mentioned might be an outlier. The upstream measurements differ far less.

It is surprising that the concentration in Hove Å can be lower than in the deposition. As previously noted, the true concentration in the wet deposition is lower than the values calculated, since the data indicates that phthalates are bound to dust particles. By filtering through the soil these dust particles are removed before the water infiltrates the river. Also, dissolved phthalates are to a certain degree removed by binding to the soil. These aspects have been investigated in another part of the project, concentrating on

soil (Thomsen & Carlsen 1997). Thus the low concentration in Hove Å may be due to a larger infiltration of ground water into this river. Finally, Hove Å - in contrast to Maglemose Å - runs through a lake located about 6 km upstream (see map Fig. 4 in Section 4). Possibly, the passage through the lake would allow particle bound phthalates to settle down to the sediment, leading to lower overall concentrations downstream of the lake.

Since the concentrations are lower than the deposition, direct pollution of the rivers with phthalates seem to be insignificant.

5.4 Waste water treatment plant

The waste water treatment plant inlet samples were analysed at an early stage of the project, as the samples from this site were used for method development. Therefore they are only representative for the winter months. Further, the high blank does not allow determination of DBP in the current concentrations. For some of the earliest samples, the recoveries were not analysed.

The WTP inlet concentrations for November 1996 and January 1997 are shown in Table 22.

Table 22 Nonylphenoles and phthalates in inlet from waste water treatment plant

| NERI No | 6.1041 1 | 6.1041 3 | 6.1041 4 | 6.1041 5 | 6.1041 6 | 7.0032 8 | 7.0032 9 | 7.0032 10 | 7.0032 11 | 7.0032 12 | Deter Limit |
|----------------------|-----------------------------------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-------------|
| | Nov 96 | | | | | Jan 97 | | | | | |
| <i>Phthalate</i> | <i>Inlet concentrations, µg/l</i> | | | | | | | | | | |
| NP | | | | | | (9) | | (22) | | | 30 |
| NPDE | na | na | na | na | na | na | na | na | na | na | |
| DBP | | | 273 | | (43) | | | | | | 60 |
| DPP | 1.2 | | | | | | | 7 | | | 0.2 |
| BBP | | | | | | | | 8 | (1) | | 2 |
| DEHP | 31 | 31 | 41 | 30 | 20 | 46 | 50 | 67 | 62 | 59 | 3 |
| DnOP | (0.3) | 1.8 | 2.7 | 39 | | 4 | | 32 | 6.5 | 2.5 | 1 |
| DnNP | | | 3.8 | | | | | 18 | | | 1 |
| DiNP | na | na | na | na | na | na | na | na | na | na | na |
| <i>Extr spike</i> | <i>Recovery, %</i> | | | | | | | | | | |
| D ₄ -DBP | na | na | 156 | 135 | 115 | na | 151 | 130 | 167 | 173 | |
| D ₄ -BBP | na | na | na | na | na | na | na | 189 | 141 | 162 | |
| D ₄ -DEHP | na | na | 115 | 144 | 126 | na | 124 | 142 | 154 | 153 | |

na = not analysed

space = not detected

Uncertain results below determination limits in ()

As can be seen, also in this case DEHP is most abundant, as must be expected since the WTP receives water from the sources already studied. The levels agree well with other Danish studies. The DEHP concentrations are thus within the range of recent studies

where levels of 18 - 95 µg/l were reported (Miljøstyrelsen 1995b & 1997a).

In Table 23 the average of the WTP concentrations and mass flow are summarised.

Table 23 Average concentrations and mass flow for the WTP

| | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | Water |
|----------------------|------------------------------------|-----------|------------|------------|------------|------------|-------------|-------------|-----------|------------------------|
| | <i>Average concentration, µg/l</i> | | | | | | | | | |
| November 1996 | | na | 63 | 0.2 | | 31 | 8.8 | 0.8 | na | |
| January 1997 | 6.2 | na | | 1.4 | 1.8 | 57 | 8.9 | 3.5 | na | |
| Total average | 3.1 | na | 32 | 0.8 | 0.9 | 44 | 8.8 | 2.1 | na | |
| | <i>Average influx, kg/y</i> | | | | | | | | | |
| November 1996 | | na | 348 | 1.3 | | 168 | 48.2 | 4.2 | na | <i>m³/y</i> |
| January 1997 | 34.1 | na | | 7.7 | 9.9 | 312 | 48.9 | 19.3 | na | |
| Total average | 17.1 | na | 174 | 4.5 | 4.9 | 240 | 48.6 | 11.7 | na | 5500000 |

As can be seen, the average concentration of the November 1996 samples are lower than the January 1997 samples. The difference for DEHP is significant by a t-test (equal variances, p=0.0004). The total average concentrations for DEHP is 44 µg/l.

A DEHP concentration in the range of 17 - 44 µg/l has recently been found in run-off from surface water to the sewer system (Miljøstyrelsen 1997b). This is a surprisingly high concentration, far greater than the deposition (0.27 - 1.6 µg/l according to Table 19), even approaching the concentration in the WTP inlet.

The average annual mass flow into the WTP, the influx, for the two months are calculated as an approximation on the basis of the annual water flow.

The last row in the table shows the total influx. It appears that the influx of DEHP amounts to about 240 kg annually

5.5 Mass flow balance for the Roskilde area.

The mass flows for the different sources are compiled in Table 24. In the first part of the table, the average annual emissions (in g per year) for the different sources (already shown in previous tables) are assembled.

In the second part of the table, these numbers are multiplied by the number of sources, arriving at a coarse estimate of the total mass flows for the town. To do this, several assumptions are implied. It is thus assumed that the contribution of all sources of the same type are of comparable magnitude, and that the samples are representative. The number of laundries is approximated, since there are only one industrial laundry, and 4 smaller laundries in the city. It is further assumed that the sources are approximately constant throughout the year. The WTP influx is assumed to be without significant seasonal variations, which has been found for sewage sludge (Miljøstyrelsen 1995b).

Table 24 Mass flow balance for total project

| Site | n | NP | NPDE | DBP | DPP | BBP | DEHP | DnOP | DnNP | DiNP | Water |
|---|----|-------|--------|--------|------|------|--------|-------|-------|-------|------------------------|
| <i>Average annual mass flow emission or influx, g/y</i> | | | | | | | | | | | <i>m³/y</i> |
| Carwash | 1 | 310 | 0.5 | 163 | 0.4 | 35 | 260 | 24 | 27 | 672 | 2371 |
| Hospital | 1 | 30 | 42 | 2714 | 20 | 6 | 1135 | 31 | 53 | | 74142 |
| Kinderg | 1 | 1491 | 9868 | | 120 | 287 | | 283 | 252 | 363 | 911 |
| Laundry | 1 | | | | | | 3650 | 154 | 137 | | 32903 |
| Deposit | 1 | 127 | | 1846 | | 307 | 3268 | 363 | | | 5813333 |
| WTP | 1 | 17050 | na | 173800 | 4510 | 4950 | 239800 | 48565 | 11715 | na | 5500000 |
| Rivers | 2 | | | 33 | 9 | 245 | 648 | 146 | 52 | | 3313457 |
| <i>Total annual mass flow emission or influx, g/y</i> | | | | | | | | | | | <i>m³/y</i> |
| Carwash | 8 | 2480 | 4 | 1302 | 3 | 277 | 2082 | 195 | 219 | 5372 | 18970 |
| Hospital | 1 | 30 | 42 | 2714 | 20 | 6 | 1135 | 31 | 53 | | 74142 |
| Kinderg | 20 | 29829 | 197357 | | 2393 | 5733 | | 5660 | 5047 | 7261 | 18220 |
| Laundry | 2 | | | | | | 7299 | 308 | 274 | | 65806 |
| Deposit | 1 | 127 | | 1846 | | 307 | 3268 | 363 | | | 5813333 |
| Sum | | 32465 | 197403 | 5862 | 2416 | 6323 | 28383 | 7172 | 6142 | 12633 | 6122083 |
| WTP | 1 | 17050 | na | 173800 | 4510 | 4950 | 239800 | 48565 | 11715 | na | 5500000 |
| Rivers | 2 | | | 33 | 9 | 245 | 648 | 146 | 52 | | 3313457 |
| <i>Percentage of sources relative to the WTP, %</i> | | | | | | | | | | | <i>%</i> |
| Carwash | 8 | 15 | - | 0.7 | 0.1 | 5.6 | 0.9 | 0.4 | 1.9 | - | 0.3 |
| Hospital | 1 | 0.2 | - | 1.6 | 0.4 | 0.1 | 0.5 | 0.1 | 0.5 | - | 1.3 |
| Kinderg | 20 | 175 | - | 0 | 53 | 116 | 0 | 12 | 43 | - | 0.3 |
| Laundry | 2 | 0 | - | 0 | 0 | 0 | 3.0 | 0.6 | 2.3 | - | 1.2 |
| Deposit | 1 | 0.7 | - | 1.1 | 0 | 6.2 | 1.4 | 0.7 | 0 | - | 106 |
| Sum | 0 | 190 | - | 3.4 | 54 | 128 | 12 | 15 | 52 | - | 111 |
| WTP | 1 | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 |
| Rivers | 2 | 0 | - | 0.02 | 0.2 | 5.0 | 0.3 | 0.3 | 0.4 | - | 60 |

There are for these reasons large uncertainties inherent in the calculations. Nevertheless, they do give an indication of the absolute and relative contribution of the sources. A more accurate estimate would need a much larger number of samples.

In the row below the sources, the sum of measured sources is calculated. This sum is to be compared with the WTP. The rivers, shown below the WTP, are not included in the sum since they do not flow through the plant.

In the third part of the table, the relative contribution of each source is calculated in percent of the WTP influx.

As can be seen from the table, the water influx to the WTP is of the same magnitude as the deposition over the 16 km² urban area.

It is clear that DEHP is the most abundant phthalate in the WTP influx.

Relative significance

The percent-part of the table gives a good overview of the relative significance of the sources. However, since NPDE, and DiNP were not measured at the WTP, the percentage of these substances cannot be calculated. Furthermore, the percentage of substances occurring in low concentrations such as BBP and DPP may be irrelevant and even misleading.

As can be seen, most of the DEHP (3%) originate from the laundries, followed by the deposition (1.4%), car wash (0.9%) and hospital (0.5%). The sum of only 12% show that only some of the sources for this compound are found. This agrees with the study of household waste water (Miljøstyrelsen 1997a), finding that about 20 - 70 % of DEHP is attributable to this source.

For DBP, the hospital seems to be most important (1.6%) followed by the deposition (1.1%).

For NP the most significant contributor seems to be the car wash (15%) and the kindergarten, as is the case for DiNP. The kindergarten results are uncertain being based on a single sample, but it is still probably a significant source.

The deposition of DBP seems to play a role. As previously noted, the deposition sampling site was located at a distance from the city centre, possibly underestimating the deposition in the city. A major difference is probably caused by the much larger concentration in the runoff into the sewer system compared to the deposition (Miljøstyrelsen 1997b).

6 Conclusions

This investigation has evaluated the absolute and relative importance of selected industries and institutions as sources of nonylphenoles and phthalates in the waste water of a medium-sized Danish city and surroundings.

The investigation comprises car wash centers, a hospital, a kindergarten and an industrial laundry (and an adhesive industry in another town). Waste water inlet from the local water treatment plant, where the emissions from the sources converge, were analysed, as well as the deposition and two rivers in the area.

The car wash results are based on 26 individual car washes, not on the outlets from the car wash centers. The kindergarten result is uncertain being based on only a single sample.

The order of importance of sources for DEHP, the most abundant phthalate in the waste water, were the laundries, followed by the deposition, the car wash centers and the hospital. These sources accounted for about 12% of the influx of this substance to the waste water plant.

For NP and DiNP, the kindergarten and the car wash centers were significant sources.

The phthalate concentrations in the deposition were very low compared to the waste water. The deposition rates of DEHP and DBP showed a seasonal variation with a minimum occurring about two months after the winter temperature minimum. Surprisingly, no influence of the wind speed and direction was seen. These findings taken together indicate a geographically even distribution of these phthalates over a large part of the Earth.

The concentrations in the two rivers were on the same or lower level as the deposition, indicating insignificant direct pollution.

The levels found agree well with other Danish studies in the cases where such data exist.

It is possible to compile a reasonable consistent balance for the mass flows of the measured substances. This shows that other sources must be present. These could be runoff from streets, waste water from washing of buildings, household waste water, industry not investigated or other sources not yet identified.

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8 Abbreviations

| | |
|----------------------|--|
| BBP | Butylbenzylphthalate |
| GC/MS | Gas chromatography/mass spectrometry |
| DBP | Dibutylphthalate |
| DEHP | Di(2-ethylhexyl)phthalate |
| DiNP | Di("iso"-nonyl)phthalate (technical mixture of different isomeric dinonylphthalates) |
| DnNP | Di(n-nonyl)phthalate |
| DnOP | Di(n-octyl)phthalate |
| DPP | Dipentylphthalate |
| D ₄ -DBP | Deuterium-labelled DBP |
| D ₄ -BBP | Deuterium-labelled BBP |
| D ₄ -DEHP | Deuterium-labelled DEHP |
| D ₄ -DnOP | Deuterium-labelled DnOP |
| HR | High resolution |
| NP | Nonylphenol |
| NPDE | Nonylphenol-diethoxylate |
| Phthalate | Phthalic acid di ester |
| WTP | Wastewater treatment plant |

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