REPORT SNO 3552-96

Occurrence of phthalates and organotins in sediments and water in Norway

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REPORT

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Abstrac

NIVA has carried out a study on the occurrence of PVC additives such as phthalates, adipates and organotins in sediment, freshwater, seawater and domestic sewage in southern Norway on the commission of Norsk Hydro, Petrochemicals Division. The actual sampling areas were possible points of discharges from factories with a known use of either phthalates or organotins or both. In addition samples were taken from clean reference areas and sewage plants. The largest source of phthalates seems to be receiving water to sewage treatment plants. 70 - 90% of the phthalates and adipates are retained in the sludge, which were dominated by DEHP. Background values from clean areas as lake Femunden were about 50 μ g/kg of DEHP, and 80 μ g/kg in marine sediments from Færder. Octyltin compounds were only found in sediments at two marine locations (Frierfjorden and Brattøya near Halden). The levels of phthalates in Norway are comparable to levels recorded in Sweden. It seems to be no contamination from industry which uses PVC additives in their production.

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Preface

The present report is financed by Norsk Hydro Petrochemicals Division, Porsgrunn. This is the first environmental study of phthalates and octyltin in Norway and should be regarded as a preliminary mapping of possible "hot spots". The areas were selected by Hydro according to production of PVC products, where phthalates or organotin compounds are part of the products. The study also includes reference areas.

All the analytical work have been carried out by Lasse Berglind. We would like to give thanks to Helena Parkman and Mikael Remberger from IVL, Sweden for their valuable help in planning the study and guidelines in the analysis. The sampling of water and sediment in freshwater has been done by Torleif Bækken, and John Arthur Berge has been responsible for the sampling of water and sediment in seawater. Both Bækken and Berge collected samples from Fuglevik sewage plant and Unni Efraimsen from VEAS sewage plant. Bjørn Braaten has been the project leader and coordinated the project. Rainer Lichtenthaler has done the quality assurance of the project. Many thanks to Hans Aksel Haugen, Hydro Porsgrunn, who has been our contact person and given us valuable help both in the planning process and the implementation of the project.

Oslo, 18 October 1996

Bjørn Braaten

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Summary

Phthalates are esters of ortho-phthalatic acid (PAEs) and are used as plasticizing agents for polyvinyl chloride (PVC). The annual consumption of phthalates in Norway is about 7000 tonnes and in addition a further 3000 tonnes may be imported, while the annual emission is estimated to 148 tonnes (Sundmark, 1995). Phthalates are among the the most abundant man-made environmental pollutants and there is an environmental concern to the high and increasing rate of PAE release to the environment. There are no monitoring data for phthalates in Norway. Several studies have, however, been performed in Sweden, that give bacground values from unpolluted sediments and water (Parkman and Remberger, 1995, 1996).

The present study has been performed by NIVA on the commission of Norsk Hydro, Petrochemical Division. Water and sediments were sampled in four lakes, Lake Mjøsa, Lake Femunden, Lake Lundevatn and Lake Heddalsvatn and from 11 localities in the Oslofjord, the Drammensfjord, the Grenlandsfjords and the Iddefjord. Samples were also taken from sludge and water from the three sewage treatment plants in the Oslofjord, VEAS, Bækkelaget and Fuglevik. The marine sites were selected as possible "hot spots" of water discharge from factories using PVC. Clean reference areas both in marine and freshwater were included in the study.

The sampling equipment and procedures prior to sampling and afterwards were designed specifically to avoid possible contamination from phthalates in the surroundings. Detailed procedures were designed for the laboratory and the phthalate analysis were planned in cooperation with IVL, Sweden. Following phthalates were analysed: DMP, DEP, DBP, BBP, DEHP, DnNP, and DnOP. In addition the adipate DEHA, and three octyltin compounds were analysed.

The largest source of phthalates seems to be receiving water (6300 - 15000 ng/l of DEHP) to sewage treatment plants. Most of the phthalates are trapped in the sludge (78500 - 113000 ug/kg dw of DEHP). The actual source for the phthalates found in the sewage is not known, neither is the degradation of the phthalates in the sludge. Except for outlet from the sewage plants, no large point source was identified.

Background values from clean areas as lake Femunden were about 50 ug/kg dw of DEHP, and the highest value, $800~\mu g/kg$, was found in Lake Heddalsvatn.

Marine reference stations contained 34 (Langesundbukta) and 80 µg/kg dw (Færder) of DEHP. The highest concentrations for DEHP in marine sediments were found outside a sewage treatment plant, 6551 µg/kg dw.

Octyltin compounds were only found at two locations, in the Frierfjord and at Brattøya near the sewage outlet for the Halden area. The relatively high value in the Frierfjord area can be related to an outlet from Norsk Hydro PVC Compound plant 5 years ago, but no discharge of water takes place today.

1. Introduction

Phthalates are esters of ortho-phthalic acid and often termed PAEs-phthalic acid esters. They are beeing produced in increasing quantities since the 1940s (Autian 1972) and few restrictions have been placed on them regarding acceptable levels in industrial wastes, liquid effluents, or work-place environments (Kohli et al. 1989). Human production and use of PAEs are first of all dependant on their quality as plastizisers and more than 90 % is directed to this use. PAEs are used as plasticizing agent for resins and polymers - especially for polyvinyl chloride (PVC). Phthalates are among the most abundant man-made environmental pollutants, and human intake per day via various routes, especially via the diet, is measured in tens of milligram (Sharman et al. 1994). Annual world production (1977) of PAEs is in the range of 1.4 x 10 9 kg (US EPA, 1980). The annual consumption of phthalates in Norway is about 7000 tonnes, and in addition a further 3000 tonnes may be imported (Sundmark, 1995). Sundmark estimated the annual emmision to 148 tonnes. Environmental concern relates to the high and increasing rate of PAE release to the environment, on their demonstrated (although frequently low) toxicity to various organisms, and on their persistence (Kohli et al. 1989). Phthalate esters as butylbenzyl phthalate (BBP) and di-n-butylphthalate (DBP) have shown to be weak estrogens on breast cancer cell (Jobling et al. 1995), whereas those derived from alkyl alcohols were not (Soto et al. 1995).

The Norwegian State Pollution Control Authority (SFT) wants to know if the processing and use of PVC products may cause pollution problems, with particular reference to possible release of phthalates and organotins. This question can be answered by an environmental study at possible point sources and reference localities in clean areas. Today, no monitoring data for phthalates exist in Norway.

In Sweden Nestle Oxo and Hydro Plast initiated a project in freshwater (Parkman and Remberger, 1995), with 22 sediment stations with increasing anthropogenic influence and point sources near polymer factories. Concentrations of DEHP varied betwen 0.01 - $0.4~\mu g/g$ dw in remote lakes and 33 and 47 $\mu g/g$ dw at point sources, a tenfold decrease compared to concentrations measured in 1983 and reported by Thurén (1986). A new Swedish study including water samples has been carried out (Parkman and Remberger 1996) parallel to the present Norwegian study. The water samples from the remote lakes had a content below 15 ng/l. The content of DEHP from Riddarfjærden, Stockholm in march 1996 was 15 ng/l compared to 3100 ng/l in september 1994. The results were presented at a Hydro seminar in april 1996.

In the fall 1996, NIVA carried out a sediment survey along the Swedish west coast (Helland et al., 1996). The sediments (analyzed by SINTEF Chemistry) showed a content of DEHP 0.3 - 8.8 μ g/g dw, 2.6 μ g/g and some were below the detection limit. Data from Danish, Swedish and Norwegian sewage plants have recently been reported by Hoffman (1996), which showed that only DEHP could be detected in considerable amounts in the sludge and outlet water. The largest uncertainty is the determination of DBP and BBP, which makes the calculation of phthalates into the sewage plant very uncertain.

In august 1995 NIVA was contacted by Norsk Hydro Petrochemicals Division, Porsgrunn about a survey of phthalates and organotin in Norwegian seawater and freshwater areas. The actual areas were possible points of discharges of water from factories. In addition it was agreed to include samples of water and sediments from sewage plants and clean reference areas. Since this was the first study of this kind in Norway, it has been necessary to develop practical methods to carry out the sampling procedure and the analytical work.

2. Materials and methods

2.1 Freshwater

2.1.1 Sampling stations

Water and sediments were sampled in four relatively big lakes in the south and south-eastern part of Norway (Figure 1). The lakes were selected to represent localities of different kinds of human influence.

Lake Lundevatn (Figure 2) is situated in the far south of Norway. The lake is mainly fed by the river Sira. The catchment area of the lake is draining nearly 2000 km² of mostly barren, partly mountainous land. About 55000 people live in this area. 28000 are found in densly populated areas (Table 1). The catchment area is strongly affected by long range pollution. The lake surface is 46 m above sea level. It has a large flat bottom area with maximum depth 314 m. Sediments were sampled at about 310 m depth (Figure 2).

Lake Heddalsvatn (Figure 3) is situated about 240 km north-east of Lake Lundevatn, and is a shallow lake. The lake surface is 16 m above sea level and the maximum depth is 54 m. The lake is fed by two main rivers, River Heddalselva and River Tinnelva. The catchment area of the lake is about 5400 km². The number of inhabitants is almost 25000. About 14500 live in densly populated areas. In the lower parts there are some agricultural activity and industry. At the north end of the lake is the small town Notodden with some industrial activity. Sediments were sampled at the maximum depth in the middle of the lake.

Lake Mjøsa (Figure 4) is situated about 200 km north-east of Lake Heddalsvatn. It is the biggest lake in Norway. The lake is fed by numerous small streams and the main river Gudbrandsdalslågen. The catchment area of the lake is about 16000 km^2 . There are three small towns, Lillehammer, Gjøvik and Hamar, and some villages situated along the lake. The area has both industrial and agricultural activity. The number of inhabitants in the catchment area of Mjøsa is about 200000, of which 54% live in densely populated areas. The lake surface is 123 m above sea level and the deepest part is close to 450 m. Water and sediments were sampled at three different sites (Figure 3): Outside Gjøvik at about 270 m, outside Hamar at 28 m and in Furnesfjorden at 42 m depth.

Lake Femunden (Figure 5) is situated about 180 km north-east of Lake Mjøsa in an area with no industry and few inhabitants. The catchment area drains 1700 km² of mostly barren, mountainous land and high altitude pine woods. Part of it is nature conservation area. The lake surface is 662 m above sea level and has a maximum depth of 150 m. Sediments were sampled at 128 m depth.

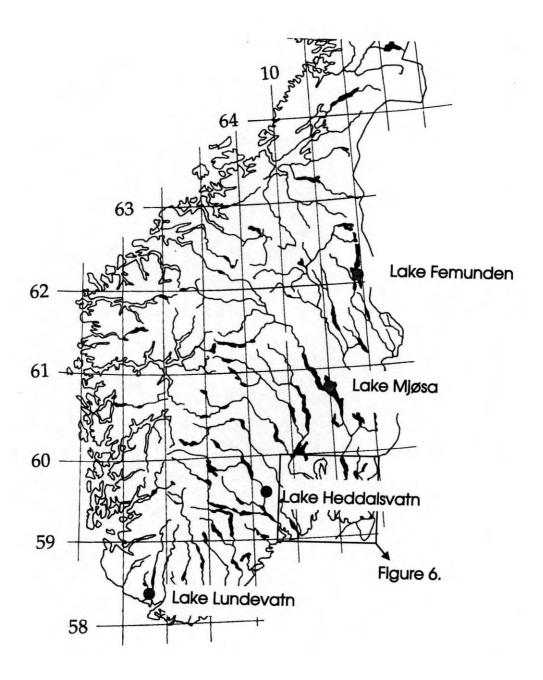


Figure 1. Samples from four big lakes in the south and south-eastern part of Norway.

 Table 1. Data from the lakes and sampling sites.

Lake Site	Sampling date	Sampling depth	Maximum depth	Above sea level	Catchmen t area	Inhabitants in catchment area	
		m	m	m	km ²	densely populated areas	sparsely populated areas
Lundevatn	11.05.96	310	314	46	1916	2800	2600
Heddalsvatn	12.05.96	54	54	16	5411	14500	9800
Mjøsa			449	123	16420	110000	93000
Hamar	04.03.96	28					
Furnesfjorden	04.03.96	42					
Gjøvik	25.02.96	270					
Femunden	24.02.96	128	150	662	1723	0	464

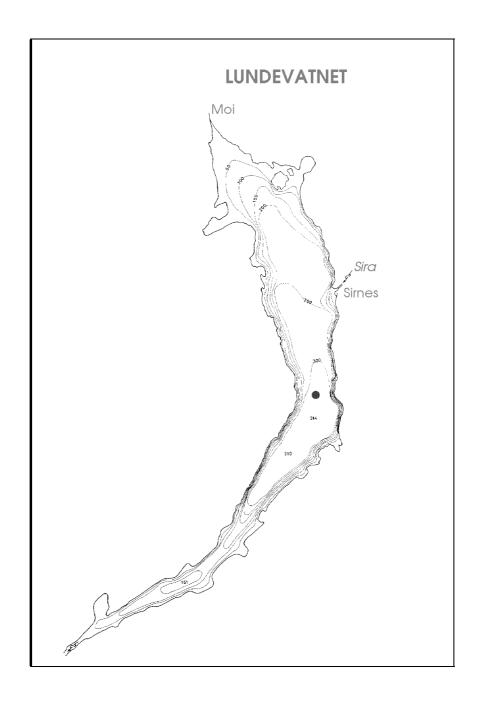


Figure 2. Lake Lundevatn with sampling station.

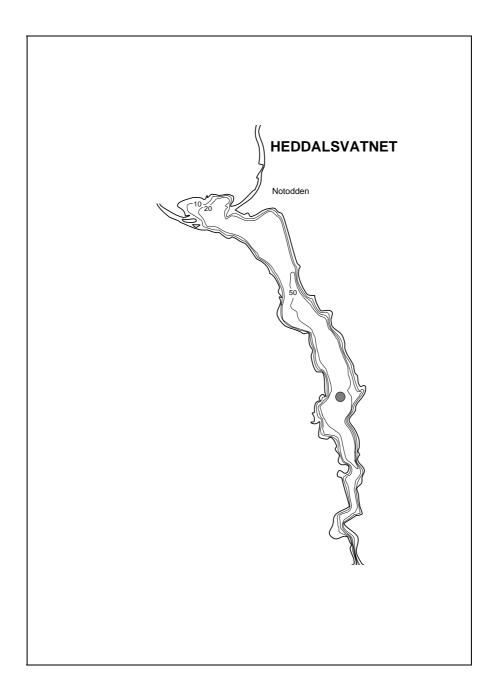


Figure 3. Lake Heddalsvatn with sampling station.

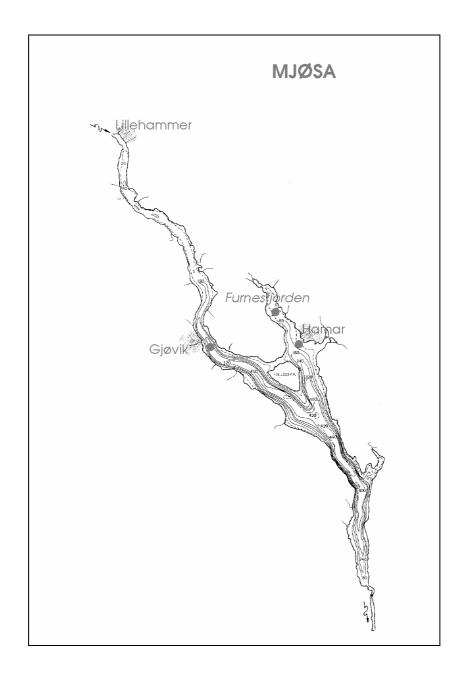


Figure 4. Lake Mjøsa with sampling stations at Gjøvik, Hamar and in Furnesfjorden.

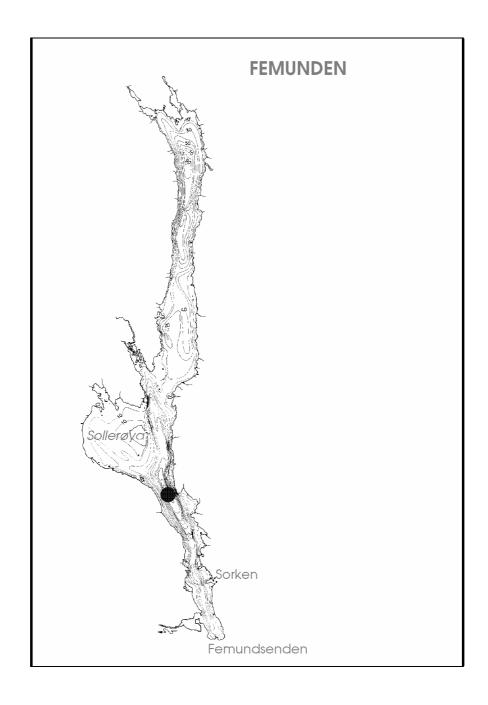


Figure 5. Lake Femunden with sampling station.

2.1.2 Sampling techniques

Sediment sampling

Limnos sediment sampler (Figure 6) was used in all lakes and at some marine sites. The sampler consists of a frame made from stainless steel, and a sampler tube usually composed of 60 rings, 1 cm long and made of polycarbonate. Part of a closing mechanism is a nylon rope outside the tube. The outer and inner diameter of the tube is 10.0 cm and 9.3 cm respectively. The sediment may be sliced in one centimetre units at any depth of the sediment core. The sampler is closed in the bottom end. It was stored and transported in an aluminium container.

The potential of the polycarbonate tube for leaching phthalates was examined. One ring was put into MilliQ-water (super - clean). It was shaken for 15 minutes in a shaking machine, and the water was analysed. Only nonquantifiable, insignificant traces were detected.

Prior to each sampling, the sampler and sampling equipment being in contact with the sediment were washed in methanol and rinsed in lake water. Surface sediments were sampled from the top 2 cm of the sediment core. Reference sediments from presumably preindustrial time were sampled at 18 - 20 cm depth. In sediment cores with less length, the deepest layer was sampled. At each station 3 samples were taken from each level. These samples were mixed to one average sample. The sediments were put into 250 ml preignited glass vials. The opening was covered by a preignited aluminium sheeting before the lid was put on.

Water was sampled at 1 m water depth in 11 or 2.51 brown, preignited glass bottles. The bottles were fastened to a steel rod by steel hose clips and quickly moved to 1 m depth and filled with water. The opening of the bottles were covered with preignited aluminium sheeting before the lid was put on. One sample was made at each station.

The samples from Lake Lundevatn and Lake Heddalsvatn were taken from an aluminium boat with outboard motor on the 11th and 12th of May 1996 respectively. Bottles, glasses and sampling equipments were transported and stored in an aluminium container. The sampling at Lake Mjøsa was made from the ice on the 26th of February and the 4th of March 1996. The sampling at Lake Femunden was made from the ice on the 25th of February 1996. Holes in the ice (ca. 0.7 m of blue ice) were made by a motor drill. Both from boat and ice the sampler was lowered and raised using a winch with steel chord.

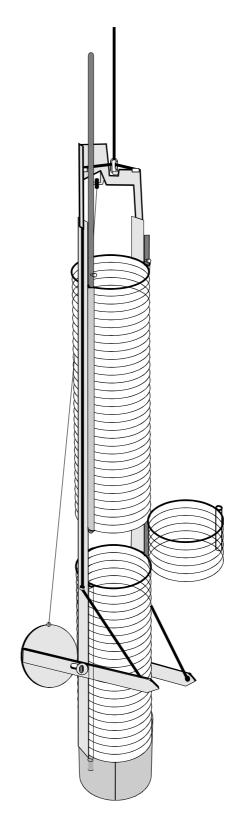


Figure 6. Sediment sampler.

2.2 Seawater

2.2.1 Sampling stations

Sediment and surface water were sampled from 11 stations (Figure 7). Three were located in the inner Oslofjord (Ormøya, Gåsøyrenna and Slemmestad). Ormøya and Slemmestad are both stations in the vicinity of the discharge point of two sewage treatment plants (Bekkelaget, VEAS) receiving sewage from the city of Oslo and some of the surrounding areas. Gåsøyrenna represents mid Inner Oslofjord conditions with no obvious point sources of discharge in the nearby area.

Gullaugbukta in the Drammensfjord is located near the sewage treatment plant at Linnestranda which receives sewage from the Lierstranda area, including sewage from Protan A/S. Holmen at the mouth of a large river (Drammenselva) is located near the discharge point of cooling water from ABB Norsk Kabel A/S.

Fuglevik in the Breiangen area is located outside a treatment plant receiving sewage from the Moss area, including sewage from Renolit Norge A/S. The station at Brattøya in the Iddefjord near the city of Halden is also located in the vicinity of the discharge point of a sewage treatment plant which also receives sewage from Rieber & Søn A/S and possibly also from Alcatel. The stations in Frierfjord, Breviksfjord and Langesundsbukta represents a gradient of antropogenic influence from the highly industrialized Frierfjord to more normal coastal conditions in the Langesund area. Færder, together with the station in Langesundsbukta, is regarded as the most remote stations (reference stations).

The stations were sampled between 27.02 - 20.03 1996 and sampling depth were between 20 - 205 m (Table 2).

Sludge and water samples were collected from three sewage treatment plants (Table 3). Sludge is particulate material from the treatment plant from which most of the water has been removed. Slurry is deluted sludge collected at an intermediate stage (before adding a polymer to promote water removal) in the treatment process.

Table 4 gives more detailed information about the type of industry and the amount of phthalates or octyltin used in tonnes/year. Information is also given about the type of product manufactured and possible discharges to the environment.

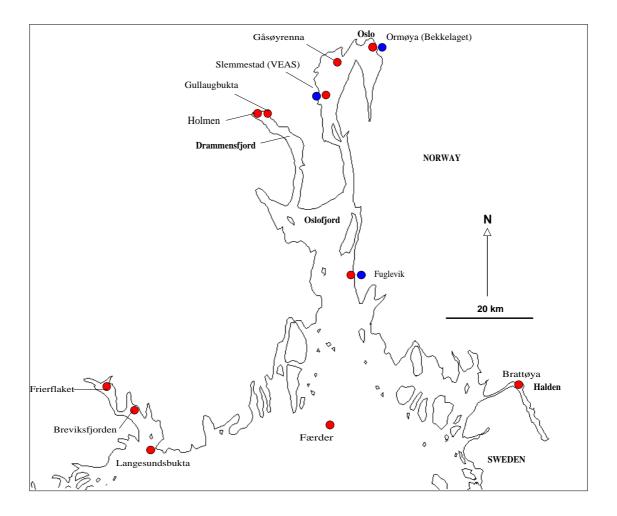


Figure 7. Sediment sampling stations (red), sewage treatment plants (blue) where sludge and water were sampled.

Table 2. Sediment sampling stations, water depth, geographic coordinates, and sampling date (name of nearby sewage treatment plant).

Station	Depth	N	E	Sampling date
	(m)			
Brattøya ¹⁾ (Halden)	20	59°07,02´N	11°11,94′E	28.02.96
Breviksfjorden	106	59°02,92′N	09°43,00′E	20.03.96
Frierflaket	23	59°06,60′N	09°37,95′E	20.03.96
Fuglevik ¹⁾ (Fuglevik)	74	59°23,07′N	10°38,70′E	19.03.96
Færder	160	58°59,72′N	10°31,35′E	19.03.96
Gullaugbukta ¹⁾	31	59°44,66´N	10°16,88′E	29.02.96
(Linnestranda)				
Gåsøyrenna	70	59°50,60′N	10°34,72′E	19.03.96
Holmen ²⁾³⁾	18	59°44,25´N	10°14,19´E	29.02.96
Langesundsbukta	205	58°58,00´N	09°48,50′E	20.03.96
Ormøya ¹⁾ (Bekkelaget)	32	59°52,72´N	10°45,72´E	27.02.96
Slemmestad ¹⁾ (VEAS))	103	59°47,69´N	10°31,55°E	19.03.96

Sediment sampled in the vicinity of the discharge from a sewage treatment plant.
 Sediment sampled in the vicinity of a cooling water discharge.

Table 3. Sewage treatment plants where sludge and water samples were collected.

Sewage treatment plant	Sampling date
Bekkelaget	13.03.96
Slemmestad (VEAS)	13.03.96
Fuglevik	28.02.96

³⁾ Several treatment plants upstream in Drammenselva.

Table 4. Additional station related information.

Station	and known to phthalates octylting		Amount of phthalates used (t/y)	Amount of octyltin used (t/y)	Product manufac- tured	
Brattøya ¹⁾ (Halden)	Near sewage treatment plant	Rieber & Søn A/S	0	180	PVC foils	
Breviksfjorden		No relevant industry known	0	0		
Frierflaket	Highly industrialized area	Norsk Hydro compound-factory	Other phthalates, 30	7 ± 0.8	PVC compounds	
Fuglevik ¹⁾ (Fuglevik)	Near sewage treatment plant	Renolit Norge A/S	DOP:1836 Discharge to air: 9 t/y DEHP	?	PVC foils	
Færder	Reference station		0	0		
Gullaugbukta ¹⁾ (Linnestranda)	Near sewage treatment plant	Protan A/S	DEHP:400 "9-11":900	0	PVC foils	
Gåsøyrenna		No relevant industry known	0	0		
Holmen ²⁾	Station at the mouth of a large river, near cooling water discharge, several treatment plants upstream	ABB Norsk Kabel A/S	DIDP: 1050 DOP: 40	0	cables containing PVC	
Langesundsbukta	Reference station		0	0		
Ormøya ¹⁾ (Bekkelaget)	Station near sewage treatment plant					
Slemmestad ¹⁾ (VEAS))	Station near sewage treatment plant					

Sediment sampled in the vicinity of the discharge from a sewage treatment plant.
 Sediment sampled in the vicinity of a cooling water discharge.

2.2.2 Sampling techniques

Sediment: Due to thick ice cover, four of the stations (Ormøya, Brattøya, Gullaugsbukta, Holmen) were sampled by lowering a sampler through a hole drilled in the ice. The equipment and procedure were the same as used for the sampling in fresh water (see page 16). The remaining stations were sampled with a corer (Niemistö, 1974). The corer was, however, modified in order to avoid contamination from plastic materials. Modifications consisted mainly of replacing the removable plastic tube where sediment is contained with a stainless steel tube and replacing the rubber plunger at the top of the sampler with a similar of aluminium.

2.3 Analysis

2.3.1 Storage

Sampling of sediments, water, sewage water and sewage sludge were carried out according to the programme planning of December 20, 1995 "Ftalater i miljøet". The samples were taken in the period 27.02 - 14.05.96. Since it is easy to contaminate the samples with phthalate from the surroundings, specially treated bottles and glass jars were used.

To control the effect of the surrounding of the samples, some of the bottles and glasses were used as blind samples. They were kept open in the sampling period and brought back to the laboratory together with the samples. The samples were kept cool until the analysis started. Further details in the sampling technique and procedures related to work up of the samples and contamination we refer to Parkman and Remberger (1995).

2.3.2 Analytical methods for phthalates/adipates

Following phthalates were analysed:

Di-methyl phthalate	DMP
Di-ethyl phthalate	DEP
Di-butyl phthalate	DBP
Butyl-benzyl-phthalate	BBP
Di-ethylhexyl phthalate	DEHP
Di-nonyl-phthalate	DnNP
Di-octhyl-phthalate	DnOP

In addition Di-ethylhexyl-adipate (DEHA) was analysed.

A surrogate standard, di-(allyl)-phthalate (DAP), was added to the samples of sediments, sewage sludge and water for control of recovery. Afterwards the sediment and sewage sludge samples were ultrasound extracted with acetonitrile. The extraction was repeated with a mixture of n-hexane and acetonitrile. The combined extract was washed with destilled water and afterwards cleaned by eluting on an ALOX-column with a mixture of n-hexane and tert-butyl-methyl ether (TBME). After evaporation, the extract was added internal standards (phenanthrene D_{10} and chrysene D_{12}) before analysis with GC/MSD in SIM.

Water samples were extracted with n-hexane in separating funnels after addition of the same surrogate standard as above. The extracts were treated in a similar way as described above before the GC/MSD analysis.

Blanks were also analysed for water and sediments.

2.3.3 Identification and quantification of phthalates

Phthalates and adipate were identified according to retention time and significant ions (SIM). Quantification was carried out according to internal standards which were added to the extracts just before analysis. The analysis of the surrogate standard in the sediment samples gave recoveries from 34% to 76%, mean value 57%. For the water samples the recoveries varied between 34% and 93%, mean value 61%. The values for recovery and blanks were used for correction of the results.

Precision at the quantification level (LOQ) for phthtalates has been calculated to 12% (Parkman and Remberger, 1995).

The method detection limit (MDL) for sediment is $6 \mu g/kg$ and for water 18 ng/l. The limit for quantification (LOQ) is $20 \mu g/kg$ and for water 60 ng/l. Parkman and Remberger (1995) describe in more detail the definition of MDL and LOQ and the Swedish values for the various phthalates.

2.3.4 Analytical methods for octyltin compounds

For further details in the work up procedures of the octyltin compounds we refer to Gremm and Frimmel (1992).

Following compounds were analysed after transformation of additives during work up procedure:

Octyltin-trichloride Dioctyltin-dichloride Trioctyltin-chloride

Extraction and developing of the three octyltin compounds were carried out in sediments and dewatered sewage sludge. After addition of a surrogate standard (tripropyltinchloride) the samples were treated with hydrochloric acid. The the samples were added ascorbic acid and tropolone (2-hydroxy-2,4-cycloheptatrien-1-on) before extraction with n-hexane in an ultrasonic bath. After drying, the extracts were added sodium sulphate and methylmagnesium bromide in an atmosphere of nitrogen for methylation to more volatile compounds. After removing the excess of the derivating agent with acid, the extracts were cleaned on silica gel with elution with n-hexane. Finally the extracts were added phenyltrimethyltin as an internal standard.

A blank was worked up together with the samples.

The analysis were carried out with a gas chromatograph connected to a mass-selective detector. Identification was carried out according to retention time and significant ions. Quantification was made due to the internal standard. The analysis of the surrogate standards gave recoveries between 108% and 115%, mean value 112%. The values for recovery and blanks were used for correction of the results.

The precision for octyltin analysis has been calculated to 9% (Gremm and Frimmel, 1992).

The detection limit for octyltin has been calculated to 12 µg/kg.

3. Results

Raw data for analyses of phthalates in water, sediment, sludge and sewage are found in appendix A.

3.1 Freshwater

3.1.1 Water

Phthalates were found in low concentrations in water samples from 1 m depth in all the lakes (Table 5). DEHP was the main phthalate in the water samples (Figure 8). At site Hamar in Lake Mjøsa no traces of any phthalate were detected. In site Furnesfjorden in Lake Mjøsa and in the reference lake Femunden nonquantifiable traces (<60 ng/l) were found. The highest concentration was observed in Mjøsa at site Gjøvik with 182 ng/l of DEHP. In Lake Heddalsvatn and Lake Lundevatn the concentrations were < 60 ng/l and 144 ng/l of DEHP, respectively.

For Lake Lundevatn long range pollution is probably the main source for phthalates. Lake Mjøsa at site Gjøvik is influenced by the river Hunnselva which is affected by different industrial activities. The observed concentration levels should, however, only be regarded indicative as the number of samples are few.

Table 5. Concentrations of the phthalate DEHP in lake water at 1 m depth in late winter 1996. The unit is ng/l.

	Lake Lundevatn	Lake Heddalsvn.	Lake Mjøsa			Lake Femunden
			Gjøvik Hamar Furnesfjord			
DEHP	144	<60	182	0	<60	<60

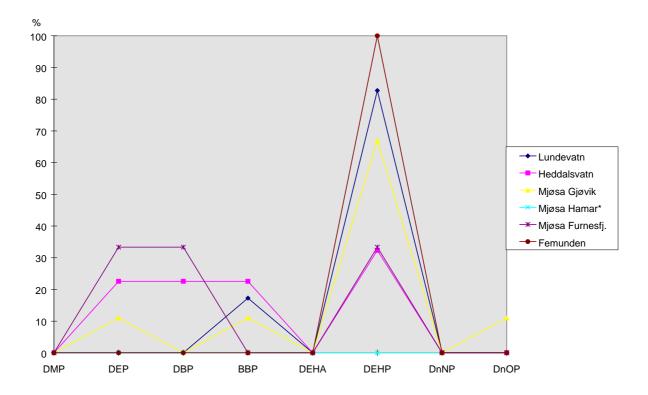


Figure 8. Occurrence of different phthalates in lake water at 1 m depth in per cent of the total amount of phthalates detected. Values below quantification limit are calculated to 50% of quantification level. (* Phthalates were not detected at Mjøsa Hamar).

3.1.2 Sediments

The most common phthalate in the sediments was DEHP. DEP, DBP, BBP, DnNP and DnOP, were occasionally detected, but except for DBP at site Gjøvik in Mjøsa, they were found in low concentrations and always made up less than 50% of the total (Figure 9 and 10). DMP was also analysed for, but never detected.

The concentrations of DEHP (in the deep reference sediments) in all sediment cores ranged from 0 to $58 \mu g/kg$, except for at site Gjøvik in Mjøsa (Figure 11). In the surface sediments the concentrations of DEHP ranged between 42 and $800 \mu g/kg$. The highest concentration of DEHP was observed in Lake Lundevatn with a concentration in the surface 14 times the reference sediment. The catchment area of this lake has no major industry. However, it is highly affected by long range pollution which is probably the source for the relatively high concentrations of DEHP in the lake sediments.

Site Gjøvik in Mjøsa was the only site where DBP was most common (Figure 12). It was, however, found in old sediments (15 cm deep) rich in cellulose filaments. This site is influenced by the river Hunnselva which previously was strongly affected by different kinds of industry. The most significant ones have been metal processing and cellulose industry. The occurrence of phthalates in relatively high concentrations in these old sediments demonstrate, however, that they may persist in sediments for many years, maybe decades.

It is assumed that the phthalates are assosiated to the organic material in the sediments. The organic content in the lake sediments varied roughly between 7 and 48% (Figure 13). At all sites, but for Mjøsa at Gjøvik, the organic content was higher in the surface sediment. In Lake Lundevatn organic content was surprisingly high. When the concentration is calculated on the basis of loss of ignition (organic content) Lake Lundevatn still had the highest concentration of DEHP. However, the difference between this lake and the other lakes is not as pronounced as when calculated on the total sediment basis (Figure 14).

The concentrations of the three analysed octyltin-species in all the lake sediments were below the detection limits of $5 \mu g/kg$ (Appendix).

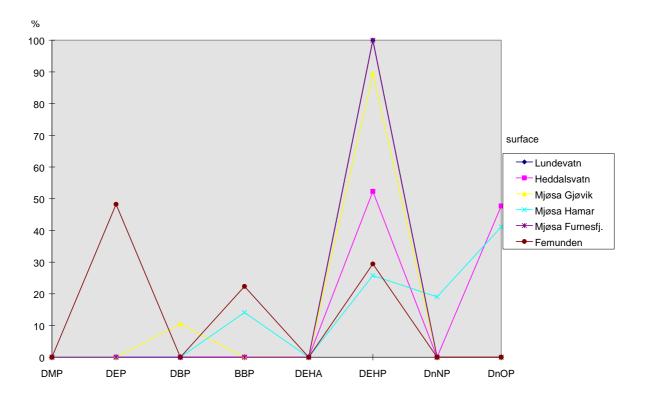


Figure 9. Occurrence of different phthalates in surface sediments of lakes in per cent of the total amount of phthalates detected. Values below quantification limit are calculated to 50% of quantification level.

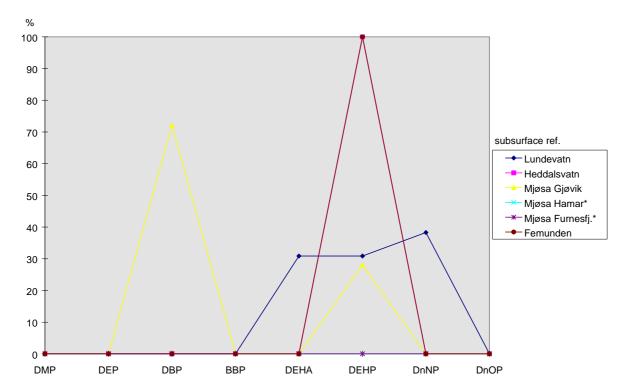


Figure 10. Occurrence of different phthalates in subsurface sediment (reference sediment) in lakes in per cent of the total amount phthalates detected. Values below quantification limit are calculated to 50% of quantification level. (* Phthalates were not detected at Mjøsa Hamar and Mjøsa Furnesfj.).

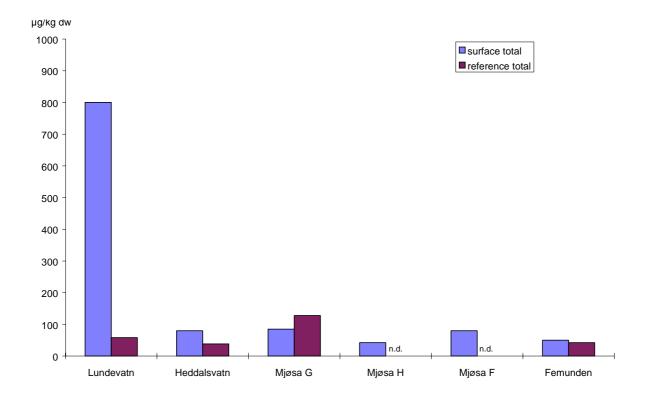


Figure 11. Concentrations of DEHP in surface sediments and subsurface sediments (reference sediment) in lakes. (n.d. pththalates not detected).

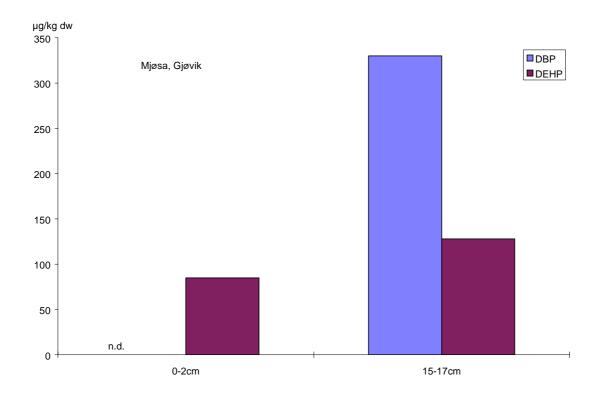


Figure 12. Concentrations of DBP and DEHP in sediments at site Gjøvik in Mjøsa. Note the higher values at the subsurface (reference) sediment. (n.d. DBP not detected).

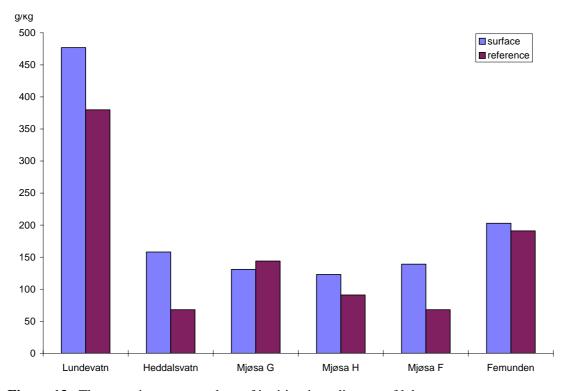


Figure 13. The organic content as loss of ignition in sediments of lakes.

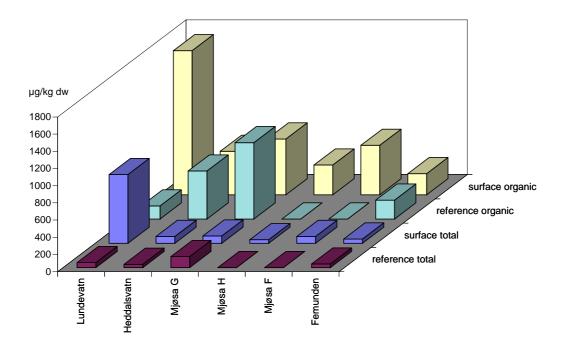


Figure 14. Concentrations of DEHP in sediments relative to total sample dry weight and to organic dry weight.

3.2 Sewage treatment plants

The incoming sewage to the treatment plants at Fuglevik and Slemmestad (VEAS) was dominated by DEHP (Figure 15.- Figure 18) whereas the incoming sewage in the treatment plant at Bekkelaget was dominated by DEP (Figure 19 and Figure 20). The concentration of DEHP was approximately two orders of magnitude lower in the discharged water than in the sewage coming in to the three treatment plants (Figure 21). The discharged water contained approximately the same order of magnitude of DEHP as the surface seawater in the vicinity of the discharge point, except for Bekkelaget (Figure 22). At Bekkelaget the surface water contained 375 ng/l wereas the discharged water contained 75 ng/l.

The retention of phthalates during the treatment process resulted in a somewhat different distribution of the individual components in the discharged water than in the incoming sewage. All three treatment plants retained approximately 99% of the DEHP associated with the incoming sewage. If the total amount of phthalates and adipates are included in the calculation, the retention would be somewhat lower for Fuglevik (69%) and Bekkelaget (90%).

The sludges from all three plants were dominated by DEHP (93 - 96%) (Figure 23). The retention of DEHP in the treatment plants resulted in high concentration of this component in the sludge (Figure 24). The concentration of DEHP ranged from $78500\,\mu\text{g/kg}$ (VEAS) to $113000\,\mu\text{g/kg}$ (Bekkelaget). The particulate material in the slurry from Fuglevik and Bekkelaget contained much less DEHP than the sludge whereas the opposite was found for the plant at Slemmestad (Figure 24). In order to facilitate water removel from the slurry, a polymer is added. The higher levels of DEHP in the sludge at Bekkelaget and Fuglevik could have been explained by possible high concentrations of DEHP in the polymer. This explanation is however not compatible with the results from VEAS where the slurry contained more DEHP than the sludge (Figure 24).

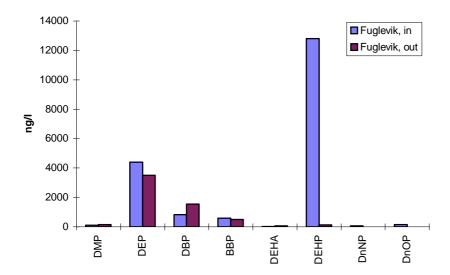


Figure 15. Contribution (ng/l) of the different compounds in incoming sewage and discharged water at the sewage plant at Fuglevik.

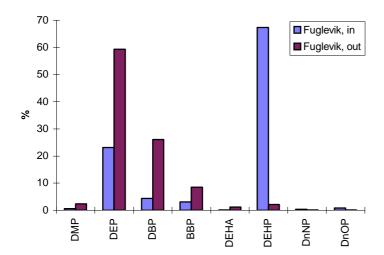


Figure 16. Contribution (%) of the different compounds in incoming sewage and discharged water at the sewage plant at Fuglrevik.

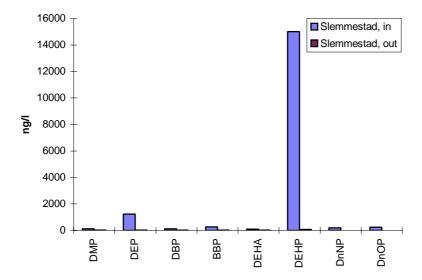


Figure 17. Contribution (ng/l) of the different compounds in incoming sewage and discharged water at the sewage plant at Slemmestad (VEAS).

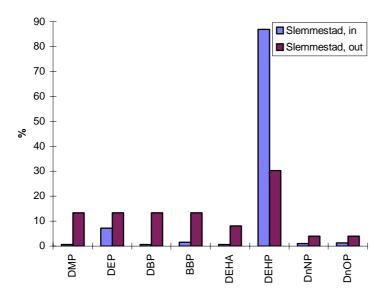


Figure 18. Contribution (%) of the different compounds in incoming sewage and discharged water at the sewage plant at Slemmestad (VEAS).

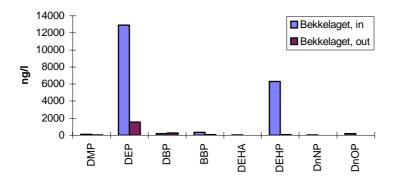


Figure 19. Contribution (ng/l) of the different compounds in incoming sewage and discharged water at the sewage plant at Bekkelaget.

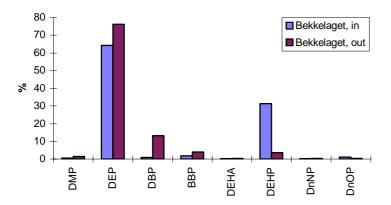


Figure 20. Contribution (%) of the different compounds in incoming sewage and discharged water at the sewage plant at Bekkelaget.

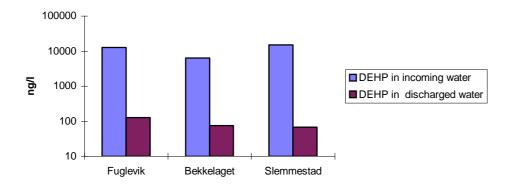


Figure 21. Concentration of DEHP in incoming sewage and discharged water from three sewage treatment plants in the Oslofjord.

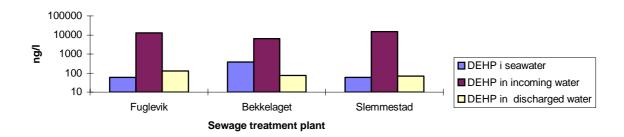


Figure 22. Concentration of DEHP in incoming sewage, discharged water and surface seawater at three sewage treatment plants in the Oslofjord.

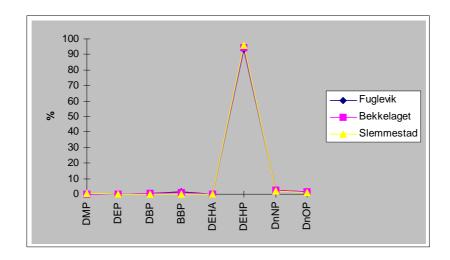


Figure 23. Contribution (%) of the different compounds in the sludge from three treatment plants.

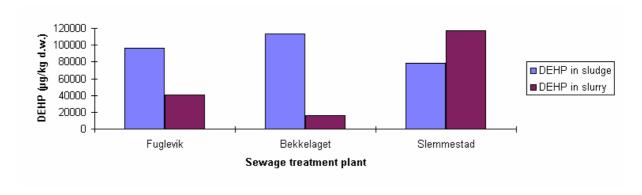


Figure 24. Concentration of DEHP in slurry and sludge (dewaterized slurry) from three sewage treatment plants in the Oslofjord.

3.3 Marine environment

3.3.1 Seawater and sediment

Traces of all the phthalates except BBP were found in one or more of the seawater samples (see raw data in Table 8 appendix A). DEHP and DMP were, however, the only components which could be quantified in surface seawater (Table 6) and only at 3 stations. The highest concentration of DEHP was found at Ormøya near the Bekkelaget treatment plant. The only other station where DEHP was quantified in the water, was at Brattøya in the vicinity of the sewage treatment plant in Halden. DMP was only quantified in the surface water in Gullaugbukta, near the Linnestranda sewage treatment plant. The concentration of DEHP found in the surface seawater in the vicinity of the discharge point from sewage treatment plants (<18-375 ng/l) was of the same order of magnitude as found in the investigated Norwegian lakes (<60-182 ng/l).

Table 6. Concentration of DEHP and DMP in surface seawater collected at sediment sampling stations.

	Fuglevik	Ormøya	Slemmestad	Gåsøyrenna	Gullaugbukta	Holmen
DEHP	<60 ¹⁾	375	<60 ¹⁾	$<18^{2)}$	$<18^{2)}$	$<60^{1)}$
DMP	$<60^{1)}$	<18	$<18^{2}$	$<18^{2}$	66	<18

	Brattøya	Færder	Langesundsbukta	Breviksfjorden	Frierflaket
DEHP	78	?	<60 ¹⁾	<18 ²⁾	<60 ¹⁾
DMP	<60	$<18^{2)}$	<18 ²⁾	<60 ¹⁾	<18 ²⁾

¹⁾ DEHP detected, concentration under the limit of quantification.

The phthalates in marine sediments were dominated by DEHP (Figure 25). The lowest concentrations of DEHP were found at the reference stations (Færder, Langesundsbukta) and the highest found in the sediment at Ormøya in the harbour area of Oslo, outside the treatment plant at Bekkelaget (Figure 26) receiving sewage from parts of the city of Oslo. The second highest concentration were found in the sediment outside the cooling water discharge at Holmen. The concentration of DEHP in the sediment on the 3 stations in the Grenlandsfjord area (Langesundsbukta, Breviksfjorden, Frierflaket) (Figure 7) increased from 34 μ /kg d.w. at the outer coastal station in Langesundsbukta to 2710 μ g/kg in the highly industrialised area in the Frierfjord (Frierflaket) (Figure 26).

Concentrations of DEHP in the sediment was 1 - 3 orders of magnitude lower than in the sludge from the nearby treatment plants (Figure 27).

The concentration of DEHP at the marine reference stations (Færder, Langesundsbukta) were approximately in the same range as found in Lake Femunden (reference station) and in Mjøsa. The highest concentrations found in the marine sediments (Bekkelaget) were however one order of magnitude higher than in Lundevann.

The fraction of the sediment with a particle size less than 63 µm was between 93% and 99% for most of the stations except for Holmen (67%) and Brattøya (88%). Normalizing the concentration of DEHP

²⁾ DEHP not detected, detction limit 18ng/l.

to the amount of fine particles in the sediment (<63 um) (Figure 28) does thus not change the distribution considerably except for Holmen.

The organic content (ash free dry weight) of the sediment varied from 18.7% (Breviksfjorden) to 5.5% (Holmen). Normalising the concentration of DEHP to the amount of organic matter (ash free dry weight) (Figure 29) shows that the highest concentration was found at Holmen and outside the sewage treatment plant at Bekkelaget.

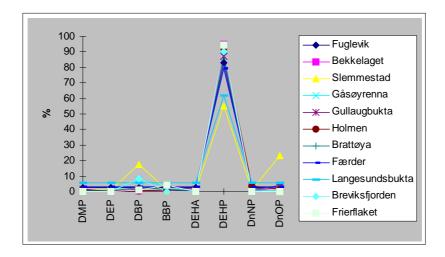


Figure 25. Contribution (%) of the different compounds in surface sediment.

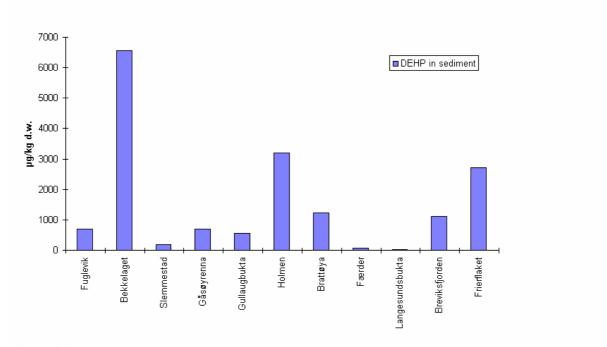


Figure 26. Concentration of DEHP in sediment.

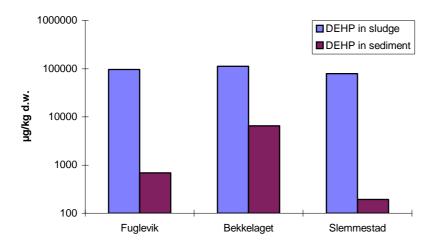


Figure 27. Concentration of DEHP in sludge from treatment plants and in sediment near the discharge point from the plant.

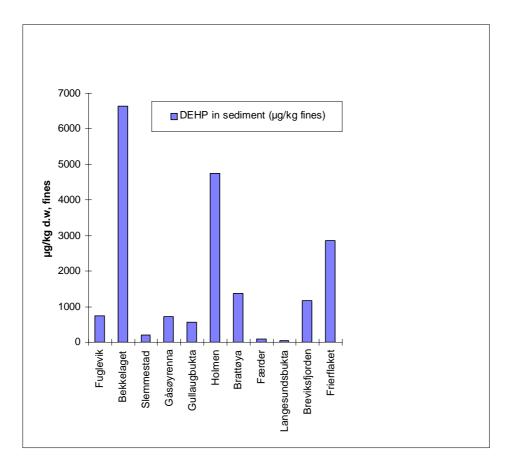


Figure 28. Normalized concentration of DEHP in sediment. Concentrations are normalized to percentage of fines in the sediment (<63um).

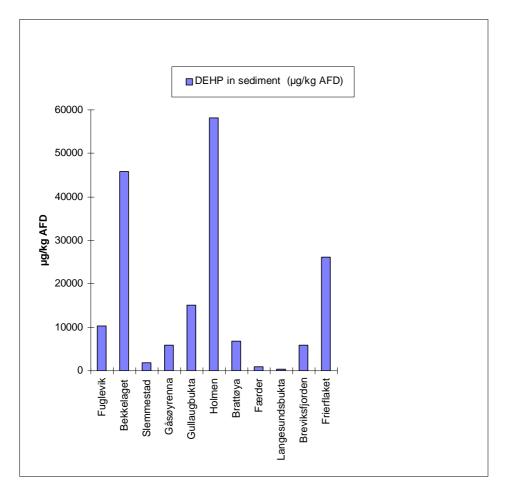


Figure 29. Normalised concentration of DEHP in sediment. Concentrations are normalized to the contents of ash free dry weight (μ g/kg AFD) in the sediment.

3.4 Octyltin

Organotins are used as stabilizers in PVC products. The trialkyltins, like TBT (tributyltin), are the most toxic ones and are used as antifouling agents in paints. The organotins in PVC - dialkyltins, are regarded as innoxious (SFT, 1993). The use of dioctyl and dibutyl tin compounds as stabilizers in PVC is estimated to 14.2 tonnes per annum (SFT, 1992).

According to (WHO, 1980) tin has only occasionally been discovered in rivers and municipal waters, and values are usually below 1 μ g/l. Values exceeding 1 μ g/l are exceptional, although values as high as 30 μ g/l have been found in drinking waters. According to earlier litterature sea water concentrations are of the order of 3 μ g/l, but more recent studies (Bruland and Franks, 1983) refers to background values in ocean water as low as < 0.01 μ g/l. Levels of dioctyltin in the environment are not known. According to Sundmark (1995) dioctyltins can be degraded by hydrolysis, photolysis and biodegradation.

All sediments from freshwater, seawater and at sewage treatment plants were analyzed. Octyltin compounds were only identified in the sediments from Brattøya and Frierflaket (Table 7). The highest concentration was found in the industrialized Frierfjord area (3200 µg/kg).

The only other positive discovery was at Brattøya which is situated near the sewage plant for the Halden area which also receives sewage from Rieber & Søn Company, who use approximately 180 t/y of octyltin.

Table 7. Concentrations of three octyltin compounds ($\mu g/kg$ d.w.) in sediment from stations where one or more compounds were detected.

Compound	Brattøya	Frierflaket
OcSnC13	N.D.	530
Oc2SnCl2	176	3200
Oc3Sn Cl	N.D.	N.D.

4. Discussion

It is difficult to infer probable background levels for phthalic acid esters (PAEs) in various aquatic environmental compartments such as freshwater, sea water, sediments and biota. PAEs, like many other anthropogenic chemical compounds, have been detected in many parts of the world at levels which cannot always be fully credited and they seem to be everywhere. Since there is no background data of phthalates in Norwegian freshwater and seawater, the best comparison is the Swedish data (Thurén, 1986, Parkman and Remberger, 1995 and 1996). Thuréns data from the two rivers early in 1980's showed much higher concentrations than observed in the present study. The DEHP concentrations at reference sites upstream discharge points ranged from 320 to 1740 ng/l in river Ronnebyåen and from 390 to 520 in the ng/l in river Svartån. Recent data from Swedish lakes and rivers (Parkman and Remberger, 1966) showed concentrations of DEHP between 7 and 193 ng/l, which is about the same magnitude as observed in the present study. The studies from Rhine river, Germany (Furtmann, 1993) were comparable to Thuréns findings from Ronnebyåen and Svartån. Kohli et al. (1989) present a list of environmental values of PAE from different parts of the world representing the various aquatic environments and biota. Surface water in Netherland contained 500 -4000 ng/l DEHP (Schwartz et al., 1979) and similar values were found in Tama river, Tokyo, Japan (Morita et al., 1974).

A study of phthalates in Swedish lakes and river sediments were made in 1994 (Parkman & Remberger, 1995). The concentrations of DEHP in general were of the same magnitude as observed in the present study. DEHP in surface sediments of their reference lakes ranged from 8 to 388 μ g/kg d.w. These concentrations were, however, significantly lower than observed in Lake Lundevatn (800 μ g/kg d.w.). As for the Lake Lundevatn, the most affected "reference" lakes, Lake Härsvatten and Lake Fräcksjön, are situated in an area influenced by long range pollution. Deposition of long range transported atmospheric phthalate may therefore be a principal source for phthalates in lakes not affected by point sources.

The inlet sewage water at Fuglevik and VEAS was dominated by DEHP, and 99% of the component was retained in the sludge or degraded. The retention was higher than comparable studies at Danish sewage plants (Grüttner et al., 1995) that measured retention of DEHP between 50 and 90%. The concentration of DEHP in Norwegian inlet sewage water (6300 - 15000 μ g/kg) was generally lower than at Danish treatment plants, and outlet water contained between 68 - 127 μ g/kg DEHP. Large variations were found in concentrations of inlet and outlet water in the Danish treatment plants. Inlet values varied between 14 000 and 49 000 ng/l and outlet values from 4000 - 33 000 ng/l. The large differences were related to analyses at various laboratories and Hoffmann (1996) points out that the uncertainty in the analysis and quantification can be ± 100 -200%. Part of the problem has been related to contamination of laboratory equipment.

The sludge from all three plants (Fuglevik, VEAS and Bekkelaget) were dominated by DEHP (93 - 96%), and concentrations ranged from 78 500 $\mu g/kg$ d.w. (VEAS) to 113 000 $\mu g/kg$ d.w. (Bekkelaget). According to Grüttner et al. (1995), the amount of DEHP in the sludge from the Danish treatment plants ranged from 2000 - 190 000 $\mu g/kg$ d.w. Data from Swedish sewage plants (Hoffman, 1996) showed values from 8700 - 148 000 $\mu g/kg$ d.w. of DEHP in the sludge, inlet values of water from 4000 - 463 400 ng/l and outlet values from 5200 - 61900 ng/l. Earlier sludge studies from Norway (Blom, 1993) gave average values of 81 500 - 594 300 $\mu g/kg$ d.w. of DEHP, where the highest value was found at Bekkelaget.

A Danish mass balance study estimated that 13 - 18 tons of phthalates from waste water treatment plants were emissioned to water in 1992 (Hoffman, 1996). The values are based upon measurements

of BBP, DBP, DEHP, DOP and DNP. The same study calculated that the total amount of phthalates that came into the sewage plants was 115 ± 82 tons $(31 \pm 34$ tons of DBP, 52 ± 74 tons BBP and 32 ± 4 tons DEHP). Only DEHP could be detected in considerable amounts in the sludge and outlet water. The largest uncertainty is in the determination of DBP and BBP, which makes the calculation of phthalates into the sewage plant highly questionable. The breakdown of DBP and BBP from the inlet water seemed to be almost 100%, while the reduction of DEHP was 25 - 75%. About 20 - 45% of the supplied DEHP can be found in the sludge (Hoffman, 1996).

Analyses of DEHP in sediment from Gothenburg area and the Swedish coast of Bohuslän (Helland et al., 1996) indicate concentrations in the range <90 - 8190 μ g/kg d.w., compared to 34 - 6551 in our investigations. The highest concentrations of DEHP along the Swedish coast was found at Eriksberg in Gothenburg (8190 μ g/kg d.w.) and near Stenungsund (7240 μ g/kg d.w.) and thus somewhat higher than found at Bekkelaget in the harbour area of Oslo.

Generally high levels of DEHP in sediment seem to be associated with antrophogenically influenced areas. The investigation along the Swedish coast demonstrates that adjacent stations may differ considerably in sediment concentrations of DEHP (two stations in the Stenungsund area contained 7240 and <300 $\mu g/kg$ d.w. respectively). In the investigation along the Swedish coast (Helland et al. 1996) the threshold for quantification of DEHP (300 $\mu g/kg$ d.w.) and the threshold for detection (90 $\mu g/kg$ d.w.) was above the concentrations found at reference stations (Færder, Langsundsbukta).

A sediment sample from the archipelago of Gothenburg contained 794 μ g/kg d.w DEHP (Parkman and Remberger, 1995) and thus in the same range as found at Fuglevik, Gåsøyrenna, Gullaugbukta and Brattøya and Breviksfjorden. Holmen is the only station having a separate discharge of water originating from the cooling of the manufactured PVC cables.

The only known values from seawater are from the surface of open water (80 μ g/kg) in the Gulf of Mexico, and from the surface of the Gulf coast (130 ng/l) (Giam et al., 1977). Most sediment samples examined for PAEs contained higher concentrations than did corresponding water samples (Pierce et al., 1980) ranging from nondetectable or less than 1.0 μ g/kg up to 218 000 μ g/kg. Ocean sediments from the Gulf of Mexico had 2 μ g/kg of DEHP and coastal sediments 6.6 μ g/kg (Giam et al., 1977). Surface water and sediment from the Mississipi Delta had mean values of 70 and 69 μ g/kg DEHP respectively.

The results from the analyses in the present study indicate that despite the considerable retention of phthalates in the sewage treatment plants, high concentrations of these compounds, mainly (DEHP) may be found in sediments near such plants. The concentration in sediments near such plants varied however. Bekkelaget is located in an area where the bottom waters often are anoxic. The low degradation of phthalates under such conditions may contribute to the especially high concentrations there. On the other hand the concentrations were considerably lower at Fuglevik which also receives sewage from Renolit Norge A/S, who use phthalates in their manufacturing process. The production process does not, however, under normal conditions include any discharge through sewage. The limited data on the discharges of phthalates from industry does not allow quantification of the contribution from industry directly. The results do, however, show that sewage treatment plants reduces the amount of phthalates introduced to the marine environment by 80 - 90%, which is in accordance with the findings in Danish waste water treatment plants (Hoffmann, 1996).

Octyltin compounds were only found at two locations, in the Frierfjord and at Brattøya near the sewage outlet for the Halden area.

The discharge may be due to the cleaning procedures of a tank containing tin stabilizers. The cleaning procedures were changed some years ago, and the outlet itself was closed approximately 5 years ago.

The relatively high value in the Frierfjorden can probably be related to an outlet of water from Norsk Hydro PVC Compound plant at Herøya. The small amount at Brattøya can probably be connected to receiving sewage from Rieber & Søn who use 180 ton octyltin per year.

As a confusion, the largest source of phthalates seems to be incoming water to sewage treatment plants, which include both domestic sewage and outlet from various industries. Since PAEs are readily sequestered, absorbed or adsorbed by organic residues and solid surfaces in aqueous environment (Kohli et al., 1989), most of the phthalates are trapped in the sludge. The actual source for the phthalates found in the sewage is not known, neither is the rate of degradation of the phthalates in the sludge.

Another important source of contamination seems to be long range transported atmospheric phthalate in freshwater lakes, but this should be regarded as a hypothesis. Except for outlet from sewage plants no large point sources were identified.

5. References

- Autian, J., 1972. Toxicity and health treats of phthalate esters: Review of the literature, Report ORNL- TIRC 72-2, Oak Ridge National Laboratory, Toxicology Information Response Center.
- Blom, H. A., 1993. Næringsstoffer og miljøgifter i slam fra norske avløpsrenseanlegg. SFT-Rapport nr. 93:26. Oslo Statens forurensningstilsyn.
- Bruland, K.W. and R.P. Franks, 1983. Mn, Ni, Cu, Zn and Cd in the Western North Atlantic. In Trace Metals in Sea Water, eds. C.S. Wong, E. Boyle, K.W. Bruland, J.d. Burton og E.D. Goldberg. Plenum, New York, pp. 395-414.
- Furtmann, K., 1993. Landesamt für Wasser und Abfall Nordrheim-Westfalen, Auf dem Draap 25, 40221 Dusseldorf 1. Report no. 6/93.
- Giam, C. S., E. Atlas, H. Chan and G. Neff, 1977. Estimation of fluxes of organic pollutants to the marine environment. Phthalate plasticizer concentration and fluxes. Rev. Int. Oceanogr. Med. Tome XLVII, pp. 79-84.
- Gremm, T.H. and F.H. Frimmel, 1992. Determination of organotin compounds in aqueous samples by means of HPGC-AED. Water Research, Vol. 26 No. 9, pp. 1163-1169.
- Grüttner, H., P. Lindegaard-Jørgensen og J. Vikelsøe, 1995. Måleprogram for phthalater på 3 danske renseanlæg. Arbeidsrapport fra Miljøstyrelsen nr. 54. København: Miljøstyrelsen.
- Helland, A., E.M. Brevik, & A. Godal, 1996. Sedimentundersøkelser i Gøteborg og Bohus läns kystvann 1995. NIVA-report nr. 3499, 64 pp + appendix.
- Hoffmann, L., 1996. Massestrømsanalyse for phthalater. Miljøprosjekt nr. 320 København Miljøstyrelsen, pp 85.
- Jobling, S., T. Reynolds, R. White, M. G. Parker and J. P. Sumpter, 1995. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environ. Health Perspect., in press.
- Kohli, J., J. F. Ryan and B. K. Afghan, 1989. Phthalate esters in the aquatic environment. Chapter 7 in: B. K. Afghan and A. S. Y. Chau (edits.). Analysis of trace organics in the aquatic environment. CRC. Press Inc., Boca Raton Florida 628 pp.
- Morita, M., H. Nakamura and S. Mimura, 1974. Phthalic acid esters in water. Water Research, vol. 8. pp. 781-788.
- Niemistö, L., 1974. A gravity corer for studies of soft sediments. Havforskningsinst. Skr. Helsinki, 238: 33-38.
- Parkman, H. & M. Remberger, 1995. Phthalates in Swedish sediments. IVL Repport Publ no. 1167, 21 pp + appendix.

- Parkman, H. and M. Remberger, 1996. Occurrence of phthalates in sediment and water in Sweden.

 Norsk Hydro Environmental Seminar in Stockholm, Radisson SAS Royal Viking Hotel, April 29, 1996. (Unpublished manuscript).
- Pierce, R.C., Mathur, S.P., Williams, T.D. and Boddington, M.J., 1980. Phthalate Esters in the Aquatic Environment. National Research Council Canada Publication NRCC No. 17583, Associate Committe on Scientific Criteria for Environmental Quality.
- Schwartz, H. E., C. J. M. Anzion, H. P. M. Van Vliet, J. W. Copius Peerebooms and U. A. Th. Brinkman, 1979. Analysis of phthalate esters in sediments from Dutch rivers by means of high performance liquid chromatography. Intern. J. Environ. Anal. Chem., Vol. 6 pp. 133-144.
- SFT, 1992. Materialstrømanalyse av tinnorganiske forbindelser. SFT-rapport 94:07.
- SFT, 1993. Miljøgifter i Norge. Priority hazardous substances in Norway. SFT-rapport 93:22.
- Sharman, M. W.A. Read, L. Castle and J. Gilbert, 1994. Levels of di-(2-ethylhexyl)phthalate and total phthalate esters in milk, cream, butter and cheese. Food Addit. Contamin., 11, 357-360.
- Soto, A. M., C. Sonnenschein, K. L. Chung, M. F. Fernandez, N. Olea and F. O. Serrano, 1995. The E-SCREEN assay as a tool to identify estrogens: An update on estrogenic environmental pollutants. Environmental Health Perspectives vol. 103, Supplement 7 oct.113 122.
- Sundmark, H B., 1995. Environmental risk asssessment of phthalates used as plasticisers for PVC. Report Hydro Research Centre, Porsgrunn Doc.no: 95P-EY4.DOC 39 pp.
- Sundmark, H.B., 1995. Risk assessment of organotin stabilizers used in PVC. Report Hydro Research Centre, Porsgrunn. Doc. no. 95P-EZ3 Doc, 24 pp.
- Thurén, A., 1986. Determination of phthalates in aquatic environments. Bull. Environ. Contam. Toxicol. 36: 33-40.
- U. S. Environmental Protection Agency, 1980. Ambient water quality criteria for phthalate esters, Report EPA 440/5-80-067. Washington, D.C.
- WHO, 1980. Tin and organotin compounds. WHO Environ. Health Criteria 15, WHO Geneva.

Appendix A.

Raw data for analyses of phthalates, adipates and octyltins in water, sediment, sludge and sewage.

Table 1. Concentration of phthalates in water samples from lakes and marine environments 1996.

	DMP	DEP	DBP	BBP	DEHA	DEHP	DnNP	DnOP
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Freshwater								
Femunden	0	0	0	0	0	<60	0	0
Mjøsa Hamar	0	0	0	0	0	0	0	0
Mjøsa Furnesfjorden	0	<60	<60	0	0	<60	0	0
Mjøsa Gjøvik	0	<60	<60	<60	0	182	0	<60
Heddalsvatn	0	<60	<60	<60	0	<60	0	0
Lundevatn	0	0	0	<60	0	144	0	0
Marine water								
Gåsøyrenna	0	<60	0	0	0	0	0	0
Slemmestad (VEAS)	0	<60	0	0	0	<60	0	0
Fuglevik	<60	<60	<60	0	<60	<60	0	0
Færder	0	0	0	0	0	*)	0	0
Langesundsbukta	0	<60	0	0	0	<60	0	0
Breviksfjorden	<60	<60	0	0	<60	0	0	<60
Frierflaket	0	<60	0	0	»	<60	0	0
Brattøya	<60	0	0	0	<60	78	0	<60
Gullaugbukta	66	0	0	0	<60	0	0	<60
Holmen	0	<60	*)	0	0	<60	0	0
Ormøya	0	0	<60	0	0	375	0	0

^{*)} Could not be determined.

Table 2. Concentrations of phthalates and octyltins in sediments of lakes and in marine environments 1996. *) Could not be determined.

	Sampling	DMP	DEP	DBP	BBP	DEHA	DEHP	DnNP	DnOP	OcSnCl ₃	Oc ₂ SnCl ₂	Oc ₃ SnCl	DW	LOI
	depth m	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	%	%
Freshwater sediments	111	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	μg/Kg	/0	/0
	120	0	02	0	20	0	50	0	0		.~	ټ.		20.2
Femunden surface	128	0	82	0	38	0	50 42	0	0	<5	<5	<5		20,3
Femunden reference	20	0	0	0	0	0		0	0	<5	<5	<5		19,1
Mjøsa Hamar surface	28	0	0	0	23	0	42	31	67	<5	<5	<5		12,1
Mjøsa Hamar reference		0	0	0	0	0	0	0	0	<5	<5	<5		9,1
Mjøsa Furnesfj. surface	42	0	0	0	0	0	80	0	0	<5	<5	<5		13,9
Mjøsa Furnesfj. reference		0	0	0	0	0	0	0	0	<5	<5	<5		6,8
Mjøsa Gjøvik surface	270	0	0	<20	0	0	85	0	0	<5	<5	<5		13,1
Mjøsa Gjøvik reference		0	0	330	0	0	128	0	0	<5	<5	<5		14,4
Heddalsvatn surface	54	0	0	0	0	0	80	0	73	<5	<5	<5		15,8
Heddalsvatn reference		0	0	0	0	0	38	0	0	<5	<5	<5		6,7
Lundevatn surface	310	0	0	0	0	0	800	0	0	<5	<5	<5		47,7
Lundevatn reference		0	0	0	0	58	58	72	0	<5	<5	<5		38
Marine surface														
sediments														
	70	0	0	60	2.4	0	600		0	_	_	~	24.0	11.7
Gråøyrenna	70	0	0	62	24	0	690	0	0	<5	<5	<5	24.9	11,7
Slemmestad (VEAS)	103	0	0	61	0	0	193	0	82	<5	<5	<5	25.8	10,2
Fuglevik	74	0	0	0	0	0	101	0	0	<5	<5	<5	45.8	6,7
Færder	100	0	0	0	0	0	80	0	0	<5	<5	<5	28.6	9
Langesundsbukta	205	0	0	0	0	0	34	0	0	<5	<5	<5	29.4	10,4
Breviksfjorden	100	0	0	102	0	0	1112	0	0	<5	<5	<5	27.3	8,7
Frierflaket	23	0	0	31	112	0	2710	0	0	530	3200	<5	36.3	10,4
Ormøya	32	<20	<20	31	74	<20	6551	<20	222	<5	<5	<5	6.3	14,3
Brattøya	20	<20	<20	32	20	<20	1221	<20	58	<5	176	<5	32.2	17,9
Gullaugbukta	31	<20	*)	<20	20	<20	556	<20	23	<5	<5	<5	58.7	3,7
Holmen	18	28	<20	<20	32	<20	3200	133	45	<5	<5	<5	51.9	5,6

Table 3. Concentration of phthalates and octyltins in the in- and outflowing water, in the sludge and in the dried sludge of sewage treatment plants.

	DMP	DEP	DBP	BBP	DEHA	DEHP	DnNP	DnOP					
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l					
Water													
Fuglevik Water inflow	115	4400	827	583	<60	12800	63	160					
Fuglevik Water outflow	142	3500	1540	500	73	127	0	0					
Bekkelaget Water inflow	103	12900	178	346	<60	6300	<60	202					
Bekkelaget Water outflow	<60	1550	270	81	0	75	0	0					
VEAS Water inflow	115	1242	115	260	106	15000	188	231					
VEAS Water outflow	<60	<60	<60	<60	0	68	0	0					
Slurry													
Fuglevik	100	43	44	630	90	40400	800	400					
Bekkelaget	<20	94	<20	630	800	15700	<20	300					
VEAS	540	<20	840	730	400	117000	1850	1600					
Sludge	DMP	DEP	DBP	BBP	DEHA	DEHP	DnNP	DnOP	OcSnCl ₃	Oc ₂ SnCl ₂	Oc ₃ SnCl	DW	LOI
	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	%	%
Fuglevik	80	<20	670	1400	<20	96000	2800	1700	<5	<5	<5	35.8	37
Bekkelaget	130	60	340	1200	<20	113000	3300	2000	<5	<5	<5	26.5	77,4
VEAS	310	<20	135	140	130	78500	1600	1030	<5	<5	<5	38.7	39