Results from the Swedish National Screening Programme 2009

Subreport 2. Dechlorane Plus

Lennart Kaj, Karin Norström, Liselott Egelrud, Mikael Remberger, Karl Lilja, Eva Brorström-Lundén B1950 November 2010

This report approved 2010-12-02 Lars-Gunnar Lindfors Scientific Director





oject title reening 2009
0
oject sponsor
vedish Environmental Protection Agency

Lennart Kaj, Karin Norström, Liselott Egelrud, Mikael Remberger, Karl Lilja, Eva Brorström-Lundén

Title and subtitle of the report

Results from the Swedish National Screening Programme 2009

Subreport 2. Dechlorane Plus

Summary

A screening study has been performed concerning Dechlorane Plus (DP). DP is a chlorinated flame retardant that has been used for a long time but has not been noticed as an environmental contaminant until recently. The main reason for its concern is its similarity to other known chloro organic chemicals with adverse effects to the environment.

DP was present in air at background locations (Råö, Aspvreten, Pallas) and in higher concentrations in urban air (Stockholm). This supports that DP is capable of long range transport and, as no traditional point sources are known, supposedly emitted from products used in urban areas, such as plastics in electrical insulators. DP was also deposited from the atmosphere. The concentration in air was in the same magnitude as for the brominated diphenyl ether congeners BDE-47 and BDE-99.

Keyword

Dechlorane Plus, air, deposition, sludge, storm water

Bibliographic data

IVL Report B1950

The report can be ordered via

Homepage: www.ivl.se, e-post: publicationservice@ivl.se, fax 08-598 563 90, or via IVL, Box 21060, 100 31 Stockholm

Summary

A screening study has been performed concerning Dechlorane Plus (DP). DP is a chlorinated flame retardant that has been used for a long time but has not been noticed as an environmental contaminant until recently. The main reason for its concern is its similarity to other known chloro organic chemicals with adverse effects to the environment.

DP is no longer on the Swedish chemical product market, but it can still be imported in products

Information on toxicity of DP to aquatic organisms is limited. DP has been shown to be of low toxicity to fish. No published studies were found on toxicity to aquatic invertebrates, algae, or sediment dwelling organisms.

DP was present in air at background locations (Råö, Aspvreten, Pallas) and in higher concentrations in urban air (Stockholm). This supports that DP is capable of long range transport and, as no traditional point sources are known, supposedly emitted from products used in urban areas, such as plastics in electrical insulators. DP was also deposited from the atmosphere. The concentration in air was in the same magnitude as for the brominated diphenyl ether congeners BDE-47 and BDE-99.

DP was found in effluent from two out of four investigated WWTPs and then in concentrations below 1 ng/l. DP was found in sludge from all four WWTPs in concentrations lower or equal to that of BDE-47.

Sammanfattning

En screeningundersökning har utförts angående Dechlorane Plus (DP). DP är ett klorerat flamskyddsmedel som har använts länge men först under senare tid uppmärksammats som en möjlig miljöförorening. Den huvudsakliga anledningen är likheterna med andra klororganiska föreningar med negativa miljöeffekter.

DP säljs inte längre på den svenska marknaden men kan importeras i produkter.

Information om DPs toxicitet på akvatiska organismer är begränsad. Det har visats att DP har låg toxicitet för fisk. Det finns inga studier av toxicitet för akvatiska invertebrater, alger eller sediment-levande organismer.

DP påvisades i luft från bakgrundslokaler (Råö, Aspvreten, Pallas) och i högre koncentrationer i urban luft (Stockholm). Detta styrker att DP kan långdistanstransporteras och, eftersom inga egentliga punktkällor är kända, troligen emitteras från produkter t ex plaster i elektrisk isolering. DP återfanns också i atmosfärisk deposition. Koncentrationerna i bakgrundsluft och deposition var i samma storleksordning som för de bromerade difenyleter kongenerna BDE-47 och BDE-99.

DP påvisades i utgående vatten från två av fyra undersökta kommunala reningsverk i koncentrationer under 1 ng/l. DP påvisades också i slam från alla fyra reningsverken i koncentrationer lägre eller lika med BDE-47.

Table of contents

Summary	
Sammanfattning	2
Table of contents	3
1 Introduction	
2 Chemical properties, fate and toxicity	6
2.1 Properties and fate	6
2.2 Toxicity	
3 Production and use	
4 Previous measurements in the environment	9
5 Sampling strategy and study sites1	0
5.1 Screening program1	
6 Methods1	0
6.1 Sampling1	
6.2 Analysis1	1
6.2.1 Sample preparation1	
6.2.2 Instrumental analysis1	
6.2.3 Quality control1	
7 Results and discussion1	2
7.1 Air1	
7.2 Atmospheric deposition1	4
7.3 Waste water treatment plants1	
7.3.1 WWTP effluent1	5
7.3.2 WWTP sludge1	
7.4 Storm water1	
7.5 DP isomers1	7
8 Conclusions1	
9 Acknowledgement1	9
10 References	9

Appendix 1. Appendix 2. Sample table, DP results. Sample table, PBDE results

1 Introduction

As an assignment from the Swedish Environmental Protection Agency, a screening study has been performed by IVL during 2009/2010. This screening includes bis(4-chlorophenyl) sulphone (BCPS), Dechlorane Plus, UV-filters, benzothiazoles, benzenediamines and benzotriazoles. These substances/substance groups are emitted and distributed in the environment via a variety of sources, e.g. different point sources and/or diffusive sources. The overall objectives of the screening studies are to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. Table 1 shows the number of the report where individual results are presented.

	_
Substance / Substance group	Sub-report #
BCPS	1
Dechlorane Plus	2
UV-filters	3
Benzothiazoles, benzenediamines	separate report
Benzotriazoles	separate report

 Table 1.
 Substances / substance groups included in the screening.

This sub-report concerns the screening of Dechlorane Plus (DP). DP is a chlorinated flame retardant that has been used for a long time but has not been noticed as an environmental contaminant until recently. The main reason for its concern is its similarity to other known chloro organic chemicals with adverse effects to the environment.

The screening of benzothiazoles, benzenediamines and benzotriazoles is carried out by IVL and Umeå University in cooperation with the project ChEmiTecs, Organic Chemicals Emitted from Technosphere Articles (www.chemitecs.se).

2 Chemical properties, fate and toxicity

2.1 Properties and fate

Dechlorane Plus® (DP) has physical properties listed in Table 2 and molecular structure depicted in Figure 1.

Property	Value	Reference
CAS no	13560-89-9	OxyChem (2007)
Systematic name	1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro- 1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro- 1,4:7,10-dimethanodibenzo(a,e)cyclooctene	ChemIDplus Advanced (2010)
Molecular formula	C ₁₈ H ₁₂ Cl ₁₂	OxyChem (2007)
Molecular weight	653.7	OxyChem (2007)
Melting point	350 °C (decomposes)	OxyChem (2007)
Vapour pressure	Negligible (0.006 mm Hg at 200°C)	OxyChem (2007) OxyChem (1997)
Density	1.8 g/cm ³	OxyChem (2007)
Water solubility	Insoluble	OxyChem (2007)
log K _{ow}	9.3	OxyChem (2007)

Table 2 Properties of DP

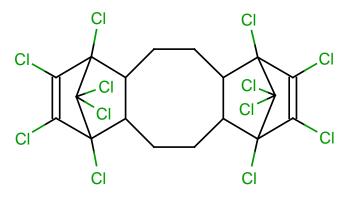


Figure 1 Molecular structure of DP.

DP occurs in two stereo isomeric forms: syn (CAS 135821-03-3) and anti (CAS 135821-74-8) (Figure 2).

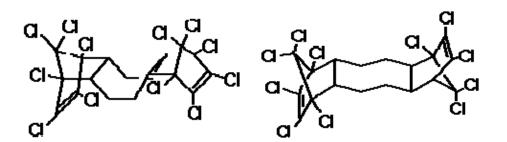


Figure 2 The two stereo isomeric forms of DP, syn (left) and anti (right).

Based on physico-chemical properties DP is expected to accumulate i soil and sediment. Assuming equal emissions to air, water and soil, a level III fugacity model estimates the distribution 91.5 % in soil, 3.4% in sediment, 5.1 % in water and 0.06 % in air (US EPA, 2010) A sorption partitioning coefficient (Kp) of 4.5 * 106 has been estimated for a water sediment system (US EPA, 2009).

Aerobic and anaerobic degradation studies have found no or low biodegradation, photodegradation is expected to be low, and DP is expected to be stable in water (US EPA, 2009).

High Kow is usually indicative of high bioaccumulation potential, but for very high Kow the relationship can be reversed. According to this and the high molecular mass DP has been predicted to have low bioaccumulation potential. However, several recent studies have shown that DP both has the potential to bioaccumulate and to biomagnify.

Tomy (2008) estimated biomagnification factors (BMFs) of 5.2 for the *syn-* and 1.9 for the *anti*isomer in a study with Rainbow Trout (*Oncorhynchus mykiss*) fed fortified food. Wu *et al.* (2010) found bioaccumulation factors (BAFs) of 135-25000 for different species from a freshwater food web. Further, they estimated a throphic magnification factor (TMF) of 10.2 for total DP for the same food web. This TMF was five times higher compared to the TMF for total PBDEs and in the same range as for total PCBs. It has also been shown that DP is transferred to Herring Gull (*Larus argentatus*) eggs, and a BMF of 600 based on concentrations measured in eggs and in the prey Alewife (*Alosa pseudoharengus*) has been estimated (Gauthier and Letcher, 2009).

DP has also been found in human serum indicating human exposure (Ren *et al.*, 2009). Highest concentrations were found in serum from electronic dismantling workers suggesting exposure through inhalation of air and dust, but DP was also found i serum from residents of a nearby region suggesting also other exposure routes.

2.2 Toxicity

Available data suggests that DP is of low acute and chronic toxicity (US EPA, 2009; Table 3). In a 28 days repeated dose study and in a 1-generation reproduction study with rats, no treatment related effects at the highest exposure dose 5000 mg/kg bw/day were found.

Organism	Test Type	Route	Reported Dose (Normalized Dose)	Effect	Source
mouse	LD50	oral	> 11848mg/kg (11848mg/kg)	behavioral somnolence (general depressed activity)	Science Reports of the Research Institutes, Tohoku University, Series C: Medicine. Vol. 36(1-4), Pg. 10, 1989.
rabbit	LD50	skin	8g/kg (8000mg/kg)		Personal Communication from L. Little,
rat	LC50	inhalation	2250mg/m3 (2250mg/m3)		Occidental Chemical Corp., Hooker Chemical Center, 360 Rainbow Blvd.
rat	LD50	oral	25gm/kg (25000mg/kg)		South, Box 728, Niagara Falls, NY 14302, May 6, 1985Vol. 06MAY1985

Table 3	Acute toxicity for DP	(ChemIDplus Advanced)

Information on toxicity of DP to aquatic organisms is limited. DP has been shown to be of low toxicity to fish. According to the IUCLID Data Set for DP submitted to US EPA, no acute toxicity to Bluegill Sunfish (*Lepomis macrochirus*) was seen at the highest tested concentration 100 mg/l (US EPA, 2009). Further, no toxicity was observed in a bioaccumulation study with the same species after exposure to 1 mg/l for 30 days. No published studies have been found on toxicity to aquatic invertebrates, algae, or sediment dwelling organisms.

3 Production and use

DP has been on the market as a flame retardant for more than 40 years. It is produced in Niagara Falls, NY, USA near the border to Canada by OxyChem (Betts 2006). This is the only known production site in North America. DP is considered a high-production-volume (HPV) chemical in USA as more than 450 tons (1 000 000 pounds) is manufactured annually. It is sold worldwide, including Europe and the Far East (Betts 2006).

DP is not produced within the European Union. The sales of DP to Europe were about 800 tons in 2000 (EU 2005).

The registered annual use of DP in Sweden is listed in Table 4. The number of preparations containing DP is also given. For Finland, Norway and Denmark no use is reported. In Sweden there was in 2008 still one preparation registered as raw material for production of plastic material, but there was no sale. An interpretation of this is that DP is no longer on the Swedish chemical product market, but it can still be imported in products (KEMI, 2010).

preparations containing DP in Sweden (SPIN, 2010									
Year	Amount, tons	Number of preparations							
2006	5	3							
2005	11	3							
2004	7	3							
2003	4	3							
1999	2	7							

Table 4Registered use of DP and total number of
preparations containing DP in Sweden (SPIN, 2010)

DP is used for coating electrical wires and cables and in computer connectors and plastic roofing materials (Betts 2006). The percent composition of DP in commercial polymer products range from 10-35% (Sverko, 2008)

DP replaced the earlier chlorinated flame retardant Dechlorane (CAS no 2385-85-5). Approximately 25% of the produced amount of this substance was used as an insecticide under the name Mirex (Report on Carcinogens).

4 Previous measurements in the environment

DP was first reported to be present in the environment in air, sediment and fish in the Great Lakes area (Hoh, 2006). A selection of previously reported environmental concentrations is cited in Table 5.

Table 5						
Matrix	Concentration	Site	Ref			
	0.41 - 490, average 34, median 2.4 pg/m ³ , n=21	50 km from production site for DP, New York, USA	Hoh 2006			
	0.31 – 134, average 9.2, median 1.9 pg/m ³ , n=22	urban area, Chicago, USA	Hoh 2006			
Air	0.25 – 21, average 3.4, median 0.83 pg/m ³ , n=12	lightly populated rural area, Ontario, USA	Hoh 2006			
	0.04 – 0.99, average 0.16, median 0.075 pg/m ³ , n=18	rural area, Michigan, USA	Hoh 2006			
	0.14 – 0.91 ng/g lipid weight, walleye (<i>Sander vitreus</i> ,)	Lake Erie, USA	Hoh 2006			
Fich	0.12 ng/g lipid weight, alewife (<i>Alosa pseudoharengus</i>)	Toronto Harbour, Canada	Tomy 2007			
Fish	36.1±35.3 ng/g lipid, fish muscle	rivers, 15 urban sites, South Korea	Kang 2010			
	1.4±1.0 ng/g lipid, fish muscle	rivers, 7 rural sites, South Korea	Kang 2010			
Birds eggs	2 – 6 ng/g w w, herring gull (<i>Laurus argentatus</i>) mean values for seven colonies for the years 1982- 2006, highest individual value 18 ng/g w w.	ing gull (<i>Laurus argentatus</i>) en colonies for the years 1982- Great Lakes, USA, Canada				
	0.061 - 8.6 ng/g DW	Lake Erie, USA	Sverko 2008			
	2.2 - 586 ng/g DW	Lake Ontario, Canada	Sverko 2008			
	2 - 5 ng/g DW	Lake Michigan, USA	Hoh 2006			
	0.033 ng/g DW, average, n=4	Lake Winnipeg, Canada	Tomy 2007			
Sediment	0.21 ng/g DW, average n=3	Lake Ontario, Canada	Tomy 2007			
	0.11±0.05 ng/g DW, average, n=6	Songhua River, within the city of Harbin, NE China	Qi 2010			
	0.04±0.05 ng/g DW, average, n=18	Songhua River, rural area, NE China	Qi 2010			

 Table 5
 Previously reported DP concentrations in different matrices

DP has been measured in serum from electronic dismantling workers in South China. Concentrations ranged from 7.8 to 465 ng/g lipid (median: 42.6). In a matched cohort from a nearby region, where fishing is the dominant industry, concentrations were lower, from 0.93 to 50.5 ng/g lipid (median: 13.7) (Ren 2009).

5 Sampling strategy and study sites

5.1 Screening program

A sampling strategy was developed in order to determine concentrations of DP in different matrices in the Swedish environment. The sampling programme was focused on atmospheric long range transport and sampling reflecting diffuse emissions from urban areas.

Air and atmospheric deposition was sampled two to four times (each sample representing one month) during a year at three background locations: Pallas in Northern Finland, Råö at the Swedish West coast and Aspvreten at the Swedish East coast 70 km SW of Stockholm. These stations are included in the national monitoring program for air and deposition. Parts of raw sample extracts from that program were, after further purification, used for analysis. Additionally, air and atmospheric deposition was sampled at an urban location in the city of Stockholm.

Effluent water and sludge from four waste water treatment plants (WWTPs) was sampled to give an indication on diffuse emissions from urban areas. Four samples of traffic related storm water was also included. The sampling programme is summarized in Table 6

Туре	Air	Depo- sition	Storm water	WWTP effluent	WWTP sludge	Total
Background areas						
Råö	4	4				8
Pallas	2	2				4
Aspvreten	3	3				6
Urban areas						
Stockholm	2	2	2	1	1	8
Göteborg				1	1	2
Umeå				1	1	2
Borås			2	1	1	4
Total	11	11	4	4	4	34

Table 6 Sampling programme

6 Methods

6.1 Sampling

Air samples were collected using high volume air samplers (HVS) with a flow of approximately 20 m³/hour. Air was sucked through a glass fibre filter (MG160, Munktell) for collection of substances in the particle phase followed by polyuretane foam (PUF) adsorbent plugs for collection of substances in the gas phase. Prior to sampling the filters were heated to 350°C, and the adsorbent was cleaned by Soxhlet extraction with acetone. The sampling was carried out for one week. Four weekly samples were later pooled to represent an average for one month. After sampling the filters and columns were wrapped in aluminium foil and stored in a freezer (-18°C) until analysis. An additional filter and column used as a field blank was sent back to the laboratory unexposed.

Both wet and dry **deposition** was collected using an open sampler (bulk sampler). The sampler consists of a 1 m² Teflon coated surface with 10 cm high edges. The bottom declines slightly to a central opening where a cassette with an adsorbent (PUF) is attached. Before sampling preheated glass fibre filters and ethanol was used to clean the surface and the adsorbent was mounted. After two weeks of sampling the adsorbent was removed and the surface was washed using preheated glass fibre filters and ethanol that was collected. The complete sample consisted of adsorbent, filters and ethanol. The deposition sample includes both compounds in the precipitation and on particles deposited to the collection surface of the sampler. This type of sampler is used for deposition measurements of organic contaminants within the Swedish national monitoring of air pollutants (Brorström-Lundén, 1996).

De-watered sludge were sampled from the anaerobic chambers into glass jars by staff at the different waste water treatment plants. The sludge was stored in a freezer (-20 °C) until analysed. Effluent waters were sampled in 1 L glass bottles. The pH was adjusted to pH 3 with H3PO4 and stored at 6 °C.

Storm water samples were provided by the Swedish Road Administration (Vägverket) and the Traffic Office (Gatukontoret) in Göteborg.

All samples are listed in Appendix 1.

6.2 Analysis

6.2.1 Sample preparation

As surrogate standard 100 ng ¹³C₁₀-DP *syn* (Cambridge Isotope Laboratories) was added to all samples.

The filter and the sorbent used for air sampling were Soxhlet-extracted with acetone for 24 hours. The acetone was diluted with ultra-pure water to a final concentration of 25 % acetone in water. The mixture was extracted twice with hexane:MTBE 9:1. The combined extracts were dried over sodium sulphate, concentrated and fractionated as described below.

Adsorbent and filters from deposition sampling were Soxhlet-extracted with acetone for 24 hours. The extract was diluted with water and extracted as described for air samples. The ethanol part of the sample was separately diluted with water and extracted as described for acetone. The combined extracts were dried over sodium sulphate, concentrated and cleaned up on a silica gel : concentrated sulphuric acid (2:1 by weight) column.

Water samples were filtered using glass fibre filters. The filtrates were solid phase extracted using isolute C18 columns (Biotage). The analyte was eluted with acetone that was subsequently diluted with water and extracted with hexane. The filter was separately extracted with acetone and hexane:MTBE. The extracts were combined and cleaned up on a silica gel : concentrated sulphuric acid (2:1 by weight) column.

Sludge was extracted with acetone and acetone:hexane. Water was added and the organic phase separated, reduced in volume and treated with concentrated sulphuric acid. Final clean-up was made using a silica gel column.

6.2.2 Instrumental analysis

Analysis was made using a 7890A gas chromatograph connected to a 7004A triple quadrupole mass spectrometer (Agilent). The analytical column, HP-5MS 30m x 250 μ m, film thickness 0.25 μ m (Agilent), was connected via a purged tee to a restrictor connected to the mass spectrometer. This arrangement made it possible to back flush the column when all analytes had been eluted. The injection was made pulsed split less at 240°C. The column temperature was held at 50°C for 1 min, increased to 325°C at 20°C /min and held at 325°C for 10 min. The transfer line was held at 290 °C. The mass spectrometer was used in SIM mode using CI ionization with methane as reaction gas. DP was monitored at m/z 653.8 with m/z 651.8 as a qualifier. ¹³C₁₀-DP was monitored at m/z 663.8.

DP technical product (Cambridge Isotope Laboratories) was used for quantification. The *syn-* and *anti-* isomers have identical response factors (Tomy, 2007). It was determined that the DP technical product contained 77% anti- isomer. A separate five point linear calibration curve was constructed for each isomer and was used for the quantification of the environmental samples.

The extracts were also analysed for BDE-47, BDE-99 and BDE-100 using the same instrument monitoring m/z 79 and m/z 81. BDE-209 and HBCD were analysed on a 15 m analytical column using EC detection.

6.2.3 Quality control

Retention times matched those of the authentic standard compounds within ± 0.2 min. The ratio of qualifier to quantifier response was within $\pm 20\%$ of the value for the standard substance. Procedural blanks were analysed together with the samples to assess possible interferences and contamination from the background.

The limit of quantification, calculated as ten times the standard deviation of the concentration measured in the blank samples, was 0.05 ng/ml sample extract for each isomer. The actual reporting limit for individual samples is dependent on extracted sample amounts, for results see Appendix 1.

7 Results and discussion

All individual results are presented in Appendix 1.

7.1 Air

The concentration of DP in air was measured at the three background locations Pallas in Northern Finland, Råö at the Swedish West coast and Aspvreten at the Swedish East coast 70 km SW of Stockholm and additionally at an urban location in the city of Stockholm. The samples represent monthly averages. The concentrations are illustrated in Figure 3.

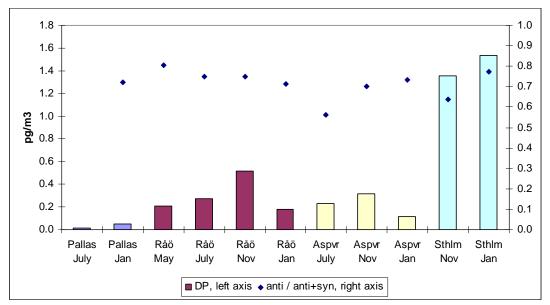


Figure 3 Concentration of DP and fraction of DP anti-isomer in air

The concentration were lowest at Pallas, 0.016 - 0.047 pg /m3, intermediate at Råö (0.18 - 0.52 pg/m3) and Aspvreten (0.12 - 0.23 pg/m3) and highest in Stockholm (1.4 - 1.5 pg/m3). This supports that DP has the ability of long distance air transport but also that it is emitted to air in Swedish urban areas. Figure 3 also illustrates the ratio of *anti* to *anti+syn* isomer. This will be further discussed in 7.5.

Comparing results from the background stations as a function of sampling month (Figure 4) gives no clear indication of an annual concentration cycle, but the number of samples is too limited to show that clearly.

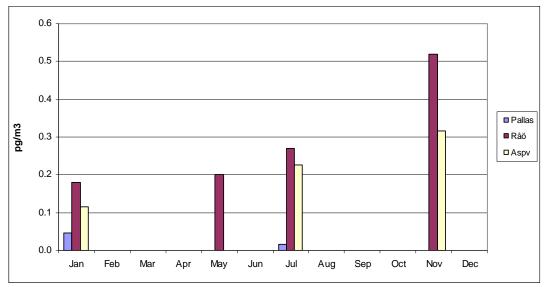


Figure 4 Concentration of DP in air at the background stations as a function of sampling month.

DP has been measured in rural and urban areas in USA (Table 5). The concentrations at Pallas were in the low range of what was measured at a rural area, while the concentrations at Råö and Aspvreten were between the median and the highest value for that area. The concentrations in Stockholm were close to the median value for the urban area Chicago.

The DP concentrations in air were fairly equal to the concentrations of the polybrominated diphenyl ether congeners BDE-47 and BDE-99, Figure 5. One exception is Pallas, July, when BDE-47 and BDE-99 concentrations were higher.

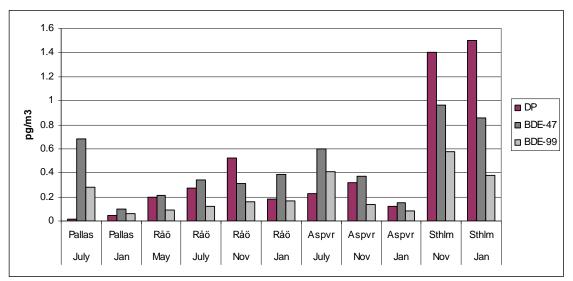


Figure 5 Concentration of DP in air compared to concentrations of BDE-47 and BDE-99.

7.2 Atmospheric deposition

The amount of atmospheric deposition of DP was measured at the three background locations Pallas, Råö and Aspvreten and at the urban location in the city of Stockholm. The samples represent monthly averages. The results are illustrated in Figure 6.

The deposition fluxes were lowest at Pallas, $0.017 - 0.025 \text{ ng/m}^2$ day, intermediate at Råö (0.11 – 0.34 ng/m² day) and Aspvreten (0.15 – 0.39 ng/m² day) and highest in Stockholm (0.50 – 0.55 ng/m² day) although the relative increase at the urban site was less than for the concentration in air.

The deposition fluxes of DP were in the same range or somewhat higher than the summed deposition of the polybrominated diphenyl ether congeners BDE-47 and BDE-99.

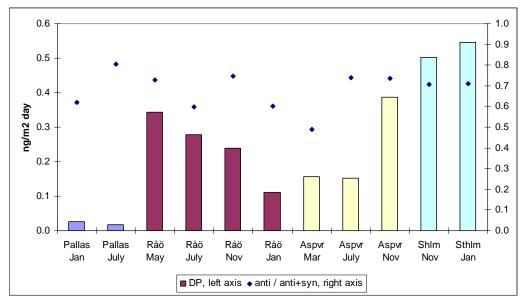


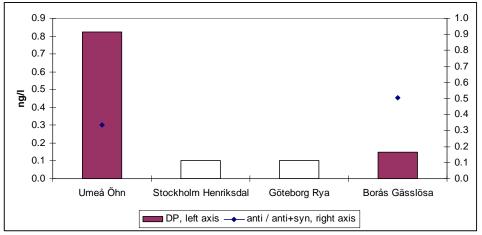
Figure 6 Flux of DP and fraction of DP anti-isomer in atmospheric deposition

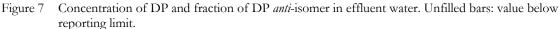
7.3 Waste water treatment plants

The DP concentrations in effluent water and sludge from four waste water treatment plants were measured. The WWTPs are all relatively large, treating water from 98 000 to 835 000 person equivalents.

7.3.1 WWTP effluent

The DP concentration in effluent water from Umeå WWTP was 0.83 ng/l and from Borås 0.15 ng/l. In effluents from Stockholm and Göteborg the DP concentration was below the reporting limit (<0.1 ng/l), Figure 7. The fraction of anti-isomer was in the range 35 - 50 %.





7.3.2 WWTP sludge

The DP concentration in the sludge from the WWTP in Umeå was 21 ng/g DW. Sludge from Borås, Göteborg and Stockholm contained 6.9 - 7.6 ng/g DW (Figure 8). The fraction of antiisomer was in the range 44 - 62 %.

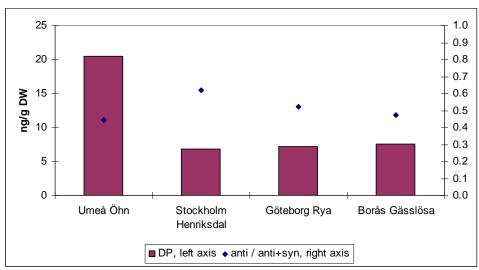


Figure 8 Concentration of DP and fraction of DP anti-isomer in sludge from WWTPs.

The concentrations of DP were somewhat lower or equal to that for the polybrominated diphenyl ether congeners BDE-47 and BDE-99. Annual averages for the four WWTPs falls in the range 27 - 45 (median 34) ng/g DW for BDE-47 and 31 - 55 (median 38) for BDE-99 for the period 2005 - 2007. The concentration of DP was fairly close to that for hexachlorobenzene (2.5 - 28, median 8.0 ng/g DW) (data from Haglund 2007, Haglund 2008).

7.4 Storm water

Two storm waters from Stockholm and two from Borås were analysed. DP was found in one from each area. The concentrations were 0.26 and 1.2 ng/l, Figure 9. The concentrations were in the same range as what was found for WWTP effluents. The reporting limit was 0.1 ng/l.

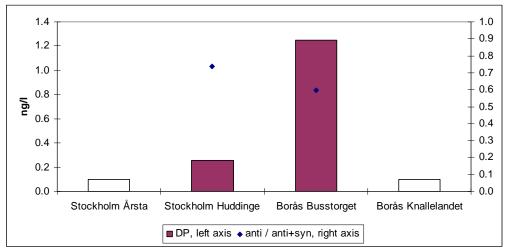
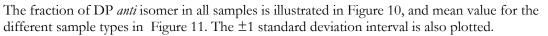


Figure 9 Concentration of DP and fraction of DP *anti*-isomer in storm water. Unfilled bars: value below reporting limit.

7.5 DP isomers

It was determined that the DP technical product contained 77% *anti-* isomer (6.2.2). This is in accordance with for example Hoh (2006) and Qiu (2007) who reported 75 - 80% and 75% respectively. Lower anti-isomer ratios for the technical product are also reported; Tomy (2007) reported 64 - 65 %. There could be differences in isomer composition in different production batches.



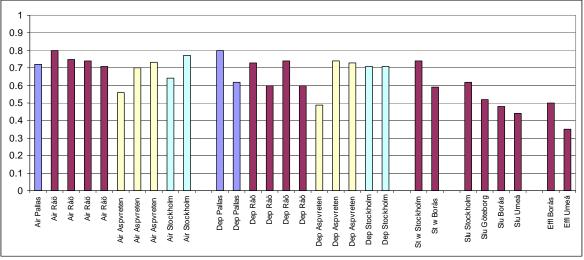


Figure 10 Fraction of DP anti-isomer

The *anti*-isomer fraction for air, deposition and storm water is close to the value for the technical product while for WWTP sludge and effluent water the fraction is lower. This is in agreement with

the suggestion that the *anti*-DP isomer should be more susceptible to biological attack relative to the less sterically hindered *syn*-DP isomer (Hoh 2006) as sludge and effluent water would have been more exposed to biological degradation than the other sample types. However, speculations on the reason for different DP isomer ratios are common in the literature and are sometimes contradicting. Factors such as differences in bioavailability and bioaccumulation and/or biotransformation efficiencies are likely to affect the isomeric composition (Gauthier 2009).

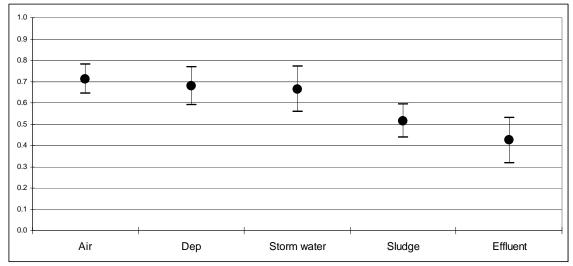


Figure 11 Fraction of DP anti-isomer for different sample types. Average, ±1 standard deviation.

8 Conclusions

DP was present in air at background locations and in higher concentrations in urban air. This supports that DP is capable of long range transport and, as no traditional point sources are known, supposedly emitted from products used in urban areas, such as plastics in electrical insulators. DP was also deposited from the atmosphere. The concentration in background air was in the same magnitude as for the brominated diphenyl ether congener BDE-47.

DP was found in effluent from two out of four investigated WWTPs and then in concentrations below 1 ng/l. DP was found in sludge from all four WWTPs in concentrations lower or equal to that of BDE-47.

DP was found in two out of four analysed storm waters in concentrations in the 1 ng/l range.

The ratio of the two isomeric forms *anti* and *syn* was equal to that of the technical product in air, deposition and storm water. In the sample types WWTP effluent and sludge, more exposed to biological degradation, the *anti*-isomer was somewhat depleted.

9 Acknowledgement

The staff at the municipal sewage treatment plants are acknowledged for their help during sampling.

This study was funded by the Swedish Environmental Protection Agency.

10 References

- Betts, K. S. (2006) A new flame retardant in the air Environ. Sci. Technol. Vol 40 1090-1091.
- Betts, K. S. (2010) Flame retardants are the suspected source of a new compund in the environment. Environ. Sci. Technol. Vol 44 546-547.
- Brorström-Lundén, E. (1996) Atmospheric Deposition of Persistent Organic Compounds to the Sea Surface. Journal of Sea Research 35: 81-90
- ChemIDplus Advanced (2010) searched for registry number 13560-89-9 2010-03-25. http://chem.sis.nlm.nih.gov/chemidplus/
- EU (2005) European Union Risk Assessment Report Hexachlorocyclopentadiene (HCCP), final draft 2005. http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/RISK_ASSESSMENT/DRAFT/R401_0512_env.pdf (accessed 2010-03-30).
- Guthier, L T; Letcher, R J (2009) Isomers of Declorane Plus flame retardant in the eggs of herring gulls *(Larus argentatus)* from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. Chemosphere 75(1) 115-120.
- Haglund, P; Olofsson U (2007) Miljöövervakning av slam. Redovisning av resultat från 2004, 2005 och 2006 års provtagningar. Miljökemi, Umeå universitet
- Haglund, P; Olofsson U (2008) Miljöövervakning av slam. Redovisning av resultat från 2007 års provtagning. Miljökemi, Umeå universitet
- Hoh, E; Zhu, L; Hites, R A (2006) Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. Environ. Sci. Technol. 40 (4) 1184-1189.
- Kang, J-H; Kim, J-C; Jin, G-Z; Park, H; Baek, S-Y; Chang, Y,S (2010) Detection of Dechlorane Plus in fish from urban-industrial rivers. Chemoshere 79, 850-854
- OxyChem (1997) Data sheet for Dechlorane Plus®, DS-0052 9/97, Occidental Chemical Corporation, Niagara Falls, NY, USA.
- OxyChem (2007) Material safety data sheet for Dechlorane Plus®, revision date May 10 2007, Occidental Chemical Corporation, Dallas, Texas, USA.
- KEMI (2010) Stellan Fisher, Swedish Chemicals Agency, personal communication 2010-06-22.
- Qi, H; Liu, L; Jia; H; Li, Y-F; Ren, N-Q; You, H; Shi, X; Fan, L; Ding, Y (2010) Dechlorane Plus in Surficial water and Sediment in a Norheastern Chinese River. Environ. Sci. Technol. 44 2305-2308

- Qiu, X; Marvin, C H; Hites, R A (2007) Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario Environ. Sci. Technol. 41 6014-6019.
- Ren, G; Yu, Z; Ma, S; Li, H; Peng, P; Sheng, G; Fu, J (2009) Determination of Dechlorane Plus in Serum from Electronics Dismantling Workers in South China. Environ. Sci. Technol. 43 9453-9457.
- Report on Carcinogens, Eleventh Edition; U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program .
- SPIN (2010) Substances in Preparations in Nordic Countries, www.kemi.se, 2010-03-26.
- Sverko, E; Tomy, G T; Marvin, C H; Zaruk, D; reiner, E; Helm, P A; Hill, B; McCarry, B E (2008) Dechlorane Plus levels in sediment of the lower Great Lakes. Environ. Sci. Technol. 42 (2) 361-366.
- Tomy, G T; Pleskach, K; Ismail, N; Whittle, D M; Helm, P A; Sverko, E; Zaruk, D; Marvin, C H (2007) Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. Environ. Sci. Technol. 41 2249-2254.
- Tomy, G T; Thomas C R; Zidane T M; Murison K E; Pleskach K; Hare J; Arsenault G; Marvin C H; Sverko E (2008) Examination of isomer specific bioaccumulation parameters and potential in vivo hepatic metabolites of *syn-* and *anti-*Dechlorane Plus isomers in juvenile Rainbow Trout (*Oncorbynchus mykiss*). Environ. Sci. Technol. 42 5562-5567.
- US EPA (2009) IUCLID Data Set for Dechlorane Plus. Date of Last Update: 07-Nov-2008. http://www.epa.gov/chemrtk/pubs/summaries/dechlorp/c15635rr3.pdf
- US EPA. (2010) Estimation Programs Interface Suite[™] for Microsoft® Windows, v 4.00. United States Environmental Protection Agency, Washington, DC, USA.
- Zhu, L; Feng, Y-L; Shoeib, M (2007) Detection of Dechlorane Plus in residential indoor dust in the city of Ottawa, Canada Environ. Sci. Technol. 41 (22) 7694-7698.

Appendix 1 Sample table, DP results

Sample ID	Туре	Area	Location	Matrix	Sampling date	DW, %	Unit	DP, syn	DP, anti	DP, total	DP anti / DP tot
MR 8368	Background	Pallas		Air	2009 July		pg/m3	<0.01	0.016	0.016	-
MR 8413	Background	Pallas		Air	2010 Jan		pg/m3	0.013	0.034	0.047	0.72
MR 8371	Background	Råö		Air	2009 May		pg/m3	0.04	0.16	0.20	0.8
MR 8365	Background	Råö		Air	2009 July		pg/m3	0.068	0.2	0.27	0.75
MR 8370	Background	Råö		Air	2009 Nov		pg/m3	0.13	0.39	0.52	0.74
MR 8364	Background	Råö		Air	2010 Jan		pg/m3	0.052	0.13	0.18	0.71
MR 8407	Background	Aspvreten		Air	2009 July		pg/m3	0.10	0.13	0.23	0.56
MR 8408	Background	Aspvreten		Air	2009 Nov		pg/m3	0.095	0.22	0.32	0.70
MR 8409	Background	Aspvreten		Air	2010 Jan		pg/m3	0.031	0.085	0.12	0.73
MR 8361	Urban	Stockholm	Valhallav. 81	Air	2009-11-05 - 12-07		pg/m3	0.49	0.86	1.4	0.64
MR 8362	Urban	Stockholm	Valhallav. 81	Air	2010-01-19 - 02-16		pg/m3	0.35	1.2	1.5	0.77
MR 8367	Background	Pallas		Deposition	2009 July		ng/m2 day	0.0033	0.013	0.017	0.80
MR 8373	Background	Pallas		Deposition	2010 Jan		ng/m2 day	0.0096	0.016	0.025	0.62
MR 8372	Background	Råö		Deposition	2009 May		ng/m2 day	0.094	0.25	0.34	0.73
MR 8366	Background	Råö		Deposition	2009 July		ng/m2 day	0.11	0.17	0.28	0.60
MR 8363	Background	Råö		Deposition	2009 Nov		ng/m2 day	0.062	0.18	0.24	0.74
MR 8374	Background	Råö		Deposition	2010 Jan		ng/m2 day	0.044	0.067	0.11	0.60
MR 8410	Background	Aspvreten		Deposition	2009 Mars		ng/m2 day	0.080	0.076	0.16	0.49
MR 8411	Background	Aspvreten		Deposition	2009 July		ng/m2 day	0.040	0.11	0.15	0.74
MR 8412	Background	Aspvreten		Deposition	2009 Nov		ng/m2 day	0.10	0.28	0.39	0.73
MR 8415	Urban	Stockholm	Valhallav. 81	Deposition	2009-11-05 - 12-07		ng/m2 day	0.15	0.36	0.50	0.71
MR 8416	Urban	Stockholm	Valhallav. 81	Deposition	2010-01-19 - 02-16		ng/m2 day	0.16	0.39	0.55	0.71
MR 8004	Urban	Borås	Gässlösa	Effluent	2009-09-29 - 09-30	1	ng/l	0.074	0.075	0.15	0.50
MR 8006	Urban	Umeå	Öhn	Effluent	2009-09-30 - 10-01		ng/l	0.55	0.280	0.83	0.35
MR 8232	Urban	Stockholm	Henriksdal	Effluent	2010-01-21		ng/l	<0.05	<0.05	<0.1	-
MR 8211	Urban	Göteborg	Rya	Effluent	2009-11-13		ng/l	<0.05	<0.05	<0.1	-

Sample ID	Туре	Area	Location	Matrix	Sampling date	DW, %	Unit	DP, syn	DP, anti	DP, total	DP anti / DP tot
MR 8005	Urban	Borås	Gässlösa	Sludge	2009-09-30	19	ng/g DW	4	3.6	7.6	0.48
MR 8007	Urban	Umeå	Öhn	Sludge	2009-10-01	31	ng/g DW	11	9.1	21	0.44
MR 8212	Urban	Göteborg	Rya	Sludge	2009-11-13	30	ng/g DW	3.5	3.8	7.2	0.52
MR 8234	Urban	Stockholm	Henriksdal	Sludge	2010-01-21	2.0	ng/g DW	2.6	4.2	6.9	0.62
MR 8039	Urban	Stockholm	Huddinge	Stormwater	2009-10-16		ng/l	0.068	0.19	0.26	0.74
MR 8038	Urban	Stockholm	Årsta	Stormwater	2009-10-16		ng/l	<0.05	<0.05	<0.1	-
MR 8156	Urban	Borås	Busstorget	Stormwater	2009-11-19		ng/l	0.051	0.74	1.2	0.59
MR 8157	Urban	Borås	Knallelandet	Stormwater	2009-11-19		ng/l	<0.05	<0.05	<0.1	-

Appendix 2 Sample table, PBDE results

Sample ID	Туре	Area	Location	Matrix	Sampling date	DW, %	Unit	BDE-47	BDE-99	BDE-100	BDE- 209	HBCD
MR 8368	Background	Pallas		Air	2009 July		pg/m3	0.68	0.28	0.06	<0.1	<0.1
MR 8413	Background	Pallas		Air	2010 Jan		pg/m3	0.10	0.06	0.02	<0.3	<0.1
MR 8371	Background	Råö		Air	2009 May		pg/m3	0.21	0.09	0.03	<0.1	<0.1
MR 8365	Background	Råö		Air	2009 July		pg/m3	0.34	0.12	0.03	0.12	<0.1
MR 8370	Background	Råö		Air	2009 Nov		pg/m3	0.31	0.16	0.04	0.29	0.44
MR 8364	Background	Råö		Air	2010 Jan		pg/m3	0.39	0.17	0.06	<0.8	<0.2
MR 8407	Background	Aspvreten		Air	2009 July		pg/m3	0.60	0.41	0.08	<1.6	interf.
MR 8408	Background	Aspvreten		Air	2009 Nov		pg/m3	0.37	0.14	0.05	<0.4	interf.
MR 8409	Background	Aspvreten		Air	2010 Jan		pg/m3	0.15	0.08	0.04	<0.4	<0.1
MR 8361	Urban	Stockholm	Valhallav. 81	Air	2009-11-05 - 12-07		pg/m3	0.96	0.58	0.11	<0.4	<0.1
MR 8362	Urban	Stockholm	Valhallav. 81	Air	2010-01-19 - 02-16		pg/m3	0.86	0.38	0.11	<0.4	<0.1
MR 8367	Background	Pallas		Deposition	2009 July		ng/m2 day	0.038	0.026	0.004	<0.1	<0.1
MR 8373	Background	Pallas		Deposition	2010 Jan		ng/m2 day	0.040	0.071	0.006	<0.17	<0.1
MR 8372	Background	Råö		Deposition	2009 May		ng/m2 day	0.11	0.065	0.018	0.51	0.25
MR 8366	Background	Råö		Deposition	2009 July		ng/m2 day	0.033	0.027	0.010	0.53	<0.1
MR 8363	Background	Råö		Deposition	2009 Nov		ng/m2 day	0.051	0.043	0.011	<0.1	<0.1
MR 8374	Background	Råö		Deposition	2010 Jan		ng/m2 day	0.028	0.030	0.011	<0.46	<0.1
MR 8410	Background	Aspvreten		Deposition	2009 Mars		ng/m2 day	0.056	0.051	<0.01	<0.57	<0.1
MR 8411	Background	Aspvreten		Deposition	2009 July		ng/m2 day	0.022	0.013	0.004	<0.14	<0.1
MR 8412	Background	Aspvreten		Deposition	2009 Nov		ng/m2 day	0.052	0.080	0.037	<015	0.35
MR 8415	Urban	Stockholm	Valhallav. 81	Deposition	2009-11-05 - 12-07		ng/m2 day	0.15	0.15	0.037	<0.15	<0.1
MR 8416	Urban	Stockholm	Valhallav. 81	Deposition	2010-01-19 - 02-16		ng/m2 day	0.070	0.070	0.026	<0.18	<0.1
MR 8004	Urban	Borås	Gässlösa	Effluent	2009-09-29 - 09-30		ng/l	0.68	0.68	0.13	3.0	1.3
MR 8006	Urban	Umeå	Öhn	Effluent	2009-09-30 - 10-01		ng/l	<0.1	<0.1	<0.1	<1.6	<0.4
MR 8232	Urban	Stockholm	Henriksdal	Effluent	2010-01-21		ng/l	<0.1	<0.1	<0.1	<1.6	<0.4
MR 8211	Urban	Göteborg	Rya	Effluent	2009-11-13		ng/l	1.1	0.88	0.17	<1.6	1.7

Sample ID	Туре	Area	Location	Matrix	Sampling date	DW, %	Unit	BDE-47	BDE-99	BDE-100	BDE- 209	HBCD
MR 8005	Urban	Borås	Gässlösa	Sludge	2009-09-30	19	ng/g DW	15	18	3.6	880	260
MR 8007	Urban	Umeå	Öhn	Sludge	2009-10-01	31	ng/g DW	20	24	4.5	59	64
MR 8212	Urban	Göteborg	Rya	Sludge	2009-11-13	30	ng/g DW	12	12	2.2	21	24
MR 8234	Urban	Stockholm	Henriksdal	Sludge	2010-01-21	2.0	ng/g DW	43	45	9.1	<10	<10
MR 8039	Urban	Stockholm	Huddinge	Stormwater	2009-10-16		ng/l	<0.1	<0.1	<0.1	<1.5	0.54
MR 8038	Urban	Stockholm	Årsta	Stormwater	2009-10-16		ng/l	0.36	0.34	<0.1	<1.5	0.81
MR 8156	Urban	Borås	Busstorget	Stormwater	2009-11-19		ng/l	0.51	0.52	0.10	<1.5	4.2
MR 8157	Urban	Borås	Knallelandet	Stormwater	2009-11-19		ng/l	<0.1	<0.1	<0.1	<1.5	2.5