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Sweco Environment
Screening Report

Screening of surface water systems adjacent to paper recycling mills

Client: Swedish Environmental Protection Agency

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Screening vid returpappersbruk inklusive toxicitetstester

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Screening of surface water systems adjacent to paper recycling mills

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Sammanfattning

Förekomst av kemiska ämnen som associeras med processer i returpappersbruk har utvärderats i vatten och sediment uppströms och nedströms fem olika returpappersbruk i Sverige. Även ekotoxikologiska effekter (Microtox®) samt hormonstörande effekter (CALUX) mättes men utan att kunna påvisa skillnader uppströms/nedströms. Med undantag för bisfenol A, som förekom i något förhöjda koncentration nedströms ett bruk, påträffades inte de flesta undersökta ämnen. Analytiska bestämningsgränser kan ha varit för höga men de koncentrationer vid vilka inga risker förväntas (PNEC) visar att de eftersökta ämnena troligen inte innebär en risk även om de skulle förekomma i koncentrationer som inte kan mätas med de aktuella metoderna. Beräkningar visar att de aktuella ämnena kan reduceras i hög grad i pappersbrukens reningsverk. Det kan vara svårt att med enstaka stickprov påvisa organiska ämnen som varierar kraftigt över tid och rum i ytvattensystem. Ämnen kan ha ersatts av ämnen med motsvarande tekniska egenskaper inom returpappersindustrin. Om man vidare vill fastställa denna industrisektors påverkan på vattenmiljön rekommenderas följande steg:

1. I samarbete med industrin och kemikalieinspektionen välja ut ämnen som kan vara av intresse för mätningar utöver de som ingått i denna studie
2. Beräkna vilka av ämnena från steg 1 som inte reduceras i lokala reningssteg
3. Mäta ämnen som kvarstår från steg 2 endast i utgående vatten från returpappersbruk
4. Med utgångspunkt från steg 3, eventuellt genomföra mätningar av ämnen som förekommer i utgående vatten i relevanta matriser i recipienter

Content

Sammanfattning

Bakgrund och metoder

Inom ramen för Naturvårdsverkets screeningprogram[1] 2012 har SWECO Environment fått i uppdrag av Naturvårdsverket att mäta och utvärdera förekomsten av ett antal ämnen som bl.a. associeras med processer i returpappersbruk. Ämnen som innefattades redovisas i nedanstående tabell.

	Ämne	CAS
Surfaktanter	4NP: 4-Nonylfenol	84852-15-3
	4NPEO1: 4-Nonylfenol (grenad)-1-etoxylat	104-35-8
	4NPEO2 : 4-Nonylfenol (grenad)-2-etoxylat	20427-84-3
	4tOP : 4-tert-Oktylfenol	140-66-9
	4tOPEO1: 4-tert-Oktylfenol-1-etoxylat	2315-67-5
	4tOPEO2: 4-tert-Oktylfenol-2-etoxylat	2315-61-9
	C10-14 Monoalkylbensen sulfon syra, natrium salt	85117-50-6
Processtillsatser	Bisfenol-A	80-05-7
	1,2-bis(3-methylfenoxyy)etan	54914-85-1
	meso-2,3-Difenylbutan	4613-11-0
	4,4'-Ditolylmetan	4957-14-6
	2,6-Diisopropylnaftalen	24157-81-1
Biocider	BNM: Bromonitrometan (nedbrytningsprodukt av bronopol)	563-70-2
	5-brom-2-hydroxyacetofenon*	1450-75-5

*endast sediment.

Utöver analyser av dessa ämnen omfattade även projektet mätningar av ekotoxikologiska effekter (Microtox®) samt hormonstörande effekter (CALUX) i recipienter nedströms och uppströms returpappersbruk..

Syftena med projektet var att:

- konstatera om och i vilken omfattning de aktuella ämnena förekommer i recipienter som berörs av returpappersbruk
- i den mån ämnen förekommer i recipienter, utvärdera om dessa utgör ett potentiellt miljöproblem
- utvärdera om ekotoxikologiska effekter förekommer nedströms de aktuella returpappersbruken

Undersökningen omfattade provtagning av vatten och sediment uppströms och nedströms fem olika returpappersbruk i södra Sverige.

[1] http://www.naturvardsverket.se/sv/Tillstandet-i-miljon/Miljoovervakning/Programomraden/Miljogiftssamordning/Screening/

Resultat och slutsatser

De flesta undersökta ämnen påträffades inte uppströms eller nedströms returpapparsbruk. Undantaget var bisfenol A som förekom i något förhöjda koncentrationer 150 m nedströms utsläppspunkten vid ett returpappersbruk. 1000 m längre nedströms var dock halter inte förhöjda relativt uppströmsmätningen. Inga skillnader i ekotoxikologiska eller hormonstörande effekter kunde påvisas mellan ytvatten uppströms och nedströms returpappersbruk.

Orsakerna till att ämnena inte påträffades är troligen:

- De analytiska bestämningsgränserna kan ha varit för höga relativt de koncentrationer som förekommer i miljön
- Beräkningar visar att de aktuella ämnena kan reduceras i hög grad i pappersbrukens interna reningsverk
- Koncentrationer av organiska ämnen i ytvattensystem varierar kraftigt över tid och rum och det kan vara mycket svårt att med enstaka prov påvisa deras förekomst
- Ämnen kan ha ersatts av ämnen med motsvarande tekniska egenskaper inom returpappersindustrin

Vidare visar jämförelser mellan ämnenas analytiska bestämningsgränser och koncentrationer vid vilka inga risker förväntas (PNEC) att de eftersökta ämnena troligen inte innebar en risk även om de skulle förekomma i koncentrationer som inte kan mätas med de aktuella analysmetoderna.

Om man vidare vill fastställa denna industrisektors påverkan på vattenmiljön rekommenderas följande steg:

1. I samarbete med industrin och kemikalieinspektionen välja ut ämnen som kan vara av intresse för mätningar utöver de som ingått i denna studie
2. Beräkna vilka av ämnens från steg 1 som inte reduceras i lokala reningssteg
3. Mäta ämnen som kvarstår från steg 2 endast i utgående vatten från returpappersbruk
4. Med utgångspunkt från steg 3, eventuellt genomföra mätningar av ämnen som förekommer i utgående vatten i relevanta matriser i recipienter

Summary

Background and methods

Within the screening program of 2012 Sweco had the assignment from the Swedish Environmental Protection Agency to measure a number of substances that are associated with e.g. paper recycling mills (Table 1-1).

Samples were collected in water and sediments, upstream and downstream at five different paper recycling mills in the southern part of Sweden (Figure 2 1, Table 2 1). Samples were analysed for all the substances in Table 1-1. Furthermore, surfaces water samples upstream and downstream the paper recycling mills were assessed for ecotoxicological effects (Microtox®) and endocrine disrupting effects (CALUX).

The objectives of the project were to:

- elucidate whether substances that are associated with paper recycling mills can be found in surface water system that receive effluents from these plants
- if the substances are found, assess whether the levels constitutes an environmental problem
- elucidate whether any toxicological effects can be seen in surface waters receiving effluents paper recycling mills.

Results and conclusions

No substances occurred at concentration >LOQ apart for Bisphenol-A in sediments adjacent to the one paper mill. The highest concentration of Bisphenol-A occurred at the closest point downstream of the mill but the concentrations were equal to upstream concentrations further downstream.

All measured concentrations or LOQs were well below predicted no effect concentrations (PNEC) and thus no direct toxic effect is expected from these substances in freshwater adjacent to paper recycling mills. No measureable ecotoxicological effect could be found with the Microtox method and the levels of estrogenic and androgenic activity were similar in all samples.

The reasons for the lack of detection in surface waters may be:

- High dilution and low concentrations
- The substances may be removed to a high degree in the waste water treatment of the paper mills.
- Temporal and spatial variability decreases the possibility of finding these substances using only a limited number of samples per paper mill

- The substances may have been replaced (in whole or partly) by other equivalent substances in the paper-recycling industry.

1 Introduction

1.1 Background

At present there is a lack of knowledge regarding the emission, distribution and exposure for many of the chemicals emitted to the environment. The aim of the screening program financed by the Swedish Environmental Protection Agency is to alleviate this lack of knowledge by estimating the occurrence of different chemicals in the environment in relevant matrices (soil, water etc.). To maximize the information gained from the screening program measurements are made in many matrices at many sites, but with few samples per site.

The Swedish EPA is responsible for the screening at the national level and selects the chemicals that are to be included. The regional county boards have the option to complement and extend the sampling program by choosing additional sampling point that are of regional interest.

Within the screening program of 2012 Sweco had the assignment from the Swedish Environmental Protection Agency to measure a number of substances that are typically associated with paper recycling mills in water bodies adjacent to these mills.

Chemical substances found in the discharged water from paper recycling mills have different origins, where some are added within the recycling process such as de-inking substances, surfactants and bleaching agents and others originates from the paper going into the recycling process. Substances included in this screening study are listed in Table 1-1.

Table 1-1. Substances included in the 2012 screening in surface waters adjacent to paper recycling mills in Sweden.

	Substance	CAS
Surfactants	4NP: 4-Nonylfenol (branched)	84852-15-3
	4NPEO1: 4-Nonylfenol (branched)-1-etoxylat	104-35-8
	4NPEO2 : 4-Nonylfenol (branched)-2-etoxylat	20427-84-3
	4tOP : 4-tert-Oktylfenol	140-66-9
	4tOPEO1: 4-tert-Oktylfenol-1-etoxylat	2315-67-5
	4tOPEO2: 4-tert-Oktylfenol-2-etoxylat	2315-61-9
	C10-14 Monoalkylbenzene sulfonic acid, sodium salt	85117-50-6
Substances from receipts etc.	Bisphenol-A	80-05-7
	1,2-bis(3-methylphenoxy)ethane	54914-85-1
	meso-2,3-Diphenylbutane	4613-11-0
	4,4'-Ditolylmetan	4957-14-6
	2,6-Diisopropylnaphthalene	24157-81-1
Biocides	BNM: Bromonitromethane (degradation product from bronopol)	563-70-2
	5-brom-2-hydroxyacetophenon*	1450-75-5

*Analyzed in sediment, not analyzed in water.

1.2 Objectives

The objectives of the project were to:

- elucidate whether possible substances that are associated with paper recycling mills can be found in surface water system that receive effluents from these plants
- if the substances are found, assess whether the levels constitutes an environmental problem
- elucidate whether any toxicological effects can be seen in surface waters receiving effluents paper recycling mills
- if substances or toxicological effects are found, elucidate to what extent this can be linked to the emissions from the plant (upstream and downstream screening).

1.3 Substance information

This section covers a brief description of usage and physicochemical properties of the substances.

1.3.1 Usage

1.3.1.1 ALKYLPHENOLS AND THEIR ETHOXYLATES

Nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs) are members of the alkylphenol ethoxylate (APE) family of non-ionic surfactants.

In paper recycling mills nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs) are used as de-inking agents in the recycling process.

The wetting properties of APEs lend themselves particularly well to degreasing activities, whilst their dispersant properties mean that they may also be used where chemical formulations need to be distributed evenly within a product or throughout a component. Both NPEs and OPEs has been used in cleaning products, paints, ink dispersants, textile and leather processing, manufacture of pulp and paper, metalworking, cosmetics and personal care products.

The import and production of 4NP in Sweden has steadily increased and is now around 140 000 kg, according to the latest available data from 2011.

1.3.1.2 LINEAR ALKYLBENZENE SULFONATE (LAS)

Within the paper recycling process Linear Alkylbenzene Sulfonate (LAS) is used as a surfactant in the de-inking step. LAS is an anionic surfactant and the primary cleaning agent used in many laundry detergents and cleaners. It was introduced in 1964 as the readily biodegradable replacement for highly branched alkylbenzene sulphonates (ABS).

LAS is a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the para position and attached to a linear alkyl chain. The linear alkyl chain has typically 10 to 13 or 14 carbon atoms. The different LAS used on the European market is represented by the list in Table 1-2.

Table 1-2. CAS and EINECS numbers of LAS in the European market (HERA 2013).

CAS No.	EINECS No.	NAME
68411-30-3	270-115-0	Benzenesulphonic acid, C10-13 alkyl derivs., sodium salts
1322-98-1	215-347-5	Sodium decylbenzenesulphonate
25155-30-0	246-680-4	Benzenedodecylsulfonic acid, sodium salt
90194-45-9	290-656-6	Benzenesulphonic acid, mono-C10-13 alkyl derivs., sodium salt
85117-50-6	285-600-2	Benzenesulphonic acid, mono-C10-14 alkyl derivs., sodium salt

1.3.1.3 BISPHENOL-A

The main source of bisphenol-A in the paper recycling process is the recycling of thermal paper which use 1 to 2 % Bisphenol A as additive for the color developer on the thermo-sensitive coating of the paper (Liao and Kannan 2011).

The import and production of Bisphenol A in Sweden peaked in 1998 with 195 000 kg and has since been relatively stable between 40 000 and 70 000 kg per year.

1.3.1.4 1,2-BIS(3-METHYLPHENOXY)ETHANE

1,2-bis(3-methylphenoxy)ethane is used as a sensitizer in thermal paper.

1.3.1.5 MESO-2,3-DIPHENYLBUTANE

Meso-2,3-Diphenylbutane (1,1´-Ditolylethane) is used in the production of thermal paper.

1.3.1.6 DI-P-TOLYLMETHANE

Di-p-tolylmethane (4,4'-Ditolylmetan) is used in the production of thermal paper.

1.3.1.7 2,6-DIISOPROPYLNAPHTHALENE

Mixtures of di-isopropyl-naphthalene (DIPN) is used in thermal copy papers as the solvent for the ink system. While it does not occur naturally, 2,6-DIPN is functionally and structurally similar to the naturally occurring plant growth regulator in potatoes (US EPA 2003).

1.3.1.8 BNM: BROMONITROMETHANE

Bromonitromethane is used in stabilized solutions as a biocide in paper mills. It is also a degradation product of other biocides used in paper mills e.g. bronopol.

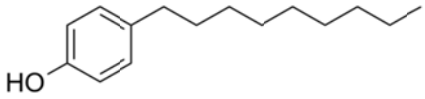
1.3.1.9 5-BROM-2-HYDROXYACETOPHENON

Probably a degradation product from biocides used in pulp and paper mills.

1.3.2 Physicochemical and toxicological properties

Below is an overview of the physicochemical and ecotoxicological properties of the substances included in this study. Where experimental data is missing, properties have been calculated with the QSAR-based software EPI Suite[2].

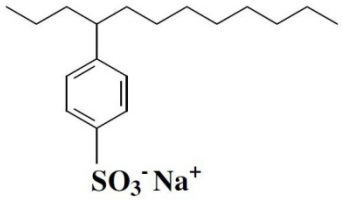
Table 1-3. Overview of physicochemical and ecotoxicological properties of nonylphenol.

Common name	**Nonylphenol**		
			
Name	Phenol, 4-nonyl-, branched		
CAS #	84852-15-3		
Physico-chemical properties [1]	Water solubility	5,7	mg/l
	Log K_{ow}	5,4	
	Henry's law constant	0,08 – 11,02	Pa*m^3/mol
	Vapour pressure	1	Pa
Ecotoxicology aquatic [1]	$PNEC_{freshwater}$	0,000614	mg/l
	$PNEC_{freshwater\_sed}$	4,62	mg/kg dw
PBT-estimate (Persistence, Bioaccumulation, Toxicity) [1]	Readily biodegradeable Bioaccumulative Toxic		
Removal in STP [2]	90.88 %		

[1] Experimental results, ECHA registration dossier
[2] Calculated

[2] EPI Suite is a free software that is made available by the US EPA (www.epa.gov). It uses quantitative structure-activity relationships (QSARs) to model properties of chemical substances.

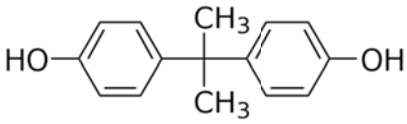
Table 1-4. Physiochemical and (Eco)toxicological properties of C10-14 Monoalkylbenzene sulfonic acid, sodium salt. Source: HERA 2013.

Common name	**Linear Alkylbenzene Sulfonate**		
			
Name	C10-14 Monoalkylbenzene sulfonic acid, sodium salt		
CAS #	85117-50-6		
			Unit
Physico-chemical properties	Water solubility [1]	250 000[1]	mg/l
	Log K_{ow} [2]	3,32	
	Henry's law constant [2]	$6,35*10^{-3}$	$Pa*m^3/mol$
	Vapour pressure [2]	$3-17*10^{-13}$	Pa
	Sorption coeff. sediment/water [1]	2-300	
Ecotoxicology aquatic	$PNEC_{freshwater}$	0,27	mg/l
	$PNEC_{sed}$	23,8	mg/kg dw
Persistence, Bioaccumulation, Toxicity (PBT)[2]	Readily biodegradeable Bioconcentration potential estimation: 87 l/kg for commercial LAS mixture, 22 l/kg för LAS in river water		
Removal in STP	80-99,9 %[1]		

[1] Experimental results

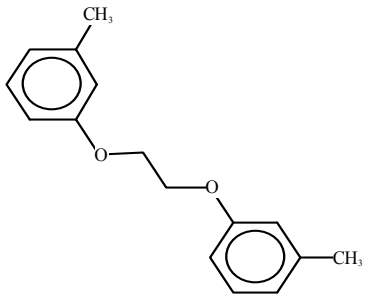
[2] Calculated

Table 1-5. Physicochemical and (Eco)toxicological properties of bisphenol-A.

Common name	**Bisphenol-A**			
				
Name	Phenol, 4,4 -(1-methylethylidene)bis-			
CAS #	80-05-7			
		Min	Max	Unit
Physico-chemical properties	Water solubility [1]	120-300		mg/l
	Log K_{ow} [1]	3.32		
	Henry's law constant [1]	$1*10^{-6}$		$Pa*m^3/mol$
	Vapour pressure [1]	$5,3*10^{-6}$		Pa
	Log K_{oc} [1]	2,53-2,85		
Ecotoxicology aquatic [3]	$PNEC_{freshwater}$	0,0016		mg/l
	$PNEC_{sed}$	0,063		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT)[2]	Readily biodegradeable Not bioaccumulating Toxic			
Removal in STP [1]	99,1 %			

[1] Experimental results
[2] Calculated
[3] EC 2008

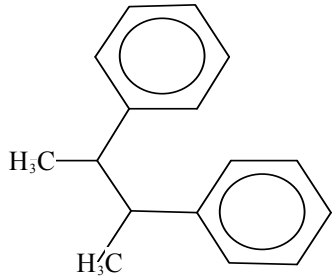
Table 1-6. Physicochemical and (Eco)toxicological properties of 1,2-bis(3-methylphenoxy)ethane.

Common name	**1,2-bis(3-methylphenoxy)ethane**		
			
Name	Benzene, 1,1'-(1,2-ethanediylbis(oxy)bis(3-meth*		
CAS #	54914-85-1		
			Unit
Physico-chemical properties [2]	Water solubility	0,293-1,70	mg/l
	Log K_{ow}	4,90	
	Henry's law constant	0,226 - 9,42	Pa*m^3/mol
	Vapour pressure	0,00263 – 0,00967	Pa
Ecotoxicology aquatic [2]	$PNEC_{freshwater}$	$6,6*10^{-5}$	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT) [2]	Persistent Very toxic		
Theoretical removal in STP	74.74%		

[1] Measured

[2] Calculated

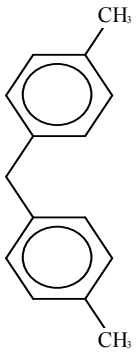
Table 1-7. Physicochemical and (Eco)toxicological properties of meso-2,3-Diphenylbutane.

Common name	**Meso-2,3-Diphenylbutane**		
			
Name	Benzene, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-, (R*,S*)-		
CAS #	4613-11-0		
			Unit
Physico-chemical properties	Water solubility	0,272 - 0,672	mg/l
	Log K_{ow}	5,57	
	Henry's law constant	35,8 - 114	Pa*m^3/mol
	Vapour pressure	0,219 – 0,511	Pa
Ecotoxicology aquatic [2]	EC_{50}	0,009	mg/l
	$PNEC_{freshwater}$	0,0015	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT) [2]	Persistent Bioaccumulative Toxic		
Theoretical removal in STP	89.3 %		

[1] Measured

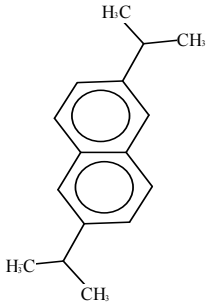
[2] Calculated

Table 1-8. Physicochemical and (Eco)toxicological properties of di-p-tolylmethane.

Common name	**4,4'-Ditolylmetan**		
			
Name	Benzene, 1,1'-methylenebis[4-metyl-		
CAS #	4957-14-6		
			Unit
Physico-chemical properties	Water solubility	0.328 - 1.976	mg/l
	Log K_{ow}	5.11	
	Henry's law constant	11.0 - 59.2	Pa*m^3/mol
	Vapour pressure	0.443 - 0.946	Pa
Ecotoxicology aquatic [2]	EC_{50}	0,030	mg/l
	$PNEC_{freshwater}$	0,0036	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT) [2]	Persistent Bioaccumulating Toxic		
Theoretical removal in STP	81.2 %		

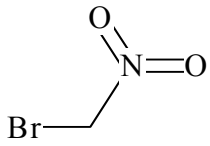
[1] Measured
[2] Calculated

Table 1-9. Physicochemical and (Eco)toxicological properties of 2,6-diisopropylnaphthalene.

Common name	**2,6-diisopropylnaphthalene**		
			
Name	Naphthalene, 2,6-bis(1-methylethyl)-		
CAS #	24157-81-1		
			Unit
Physico-chemical properties [2]	Water solubility	0.1146 - 0.2421	mg/l
	Log K_{ow}	6.081	
	Henry's law constant	197 - 202	Pa*m^3/mol
	Vapour pressure	0.0544 - 0.137	Pa
Ecotoxicology aquatic [2]	EC_{50}	0,002	mg/l
	$PNEC_{freshwater}$	0,0002	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT) [2]	Persistent Bioaccumulating Toxic		
Theoretical removal in STP	92.7		

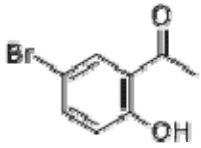
[1] Measured
[2] Calculated

Table 1-10. Physicochemical and (Eco)toxicological properties of BNM: Bromonitromethane (degradation product from bronopol).

Common name	**BNM: Bromonitromethane**		
			
Name	Bromonitromethane		
CAS #	563-70-2		
			Unit
Physico-chemical properties	Water solubility	18680 - 42740	mg/l
	Log K_{ow}	0,31	
	Henry's law constant	0,492	$Pa*m^3/mol$
	Vapour pressure	512 - 743	Pa
Ecotoxicology aquatic[2]	EC_{50}	723	mg/l
	$PNEC_{freshwater}$	11,6	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT)[2]	Not persistent Not bioaccumulating Not toxic		
Theoretical removal in STP	2.12 %		

[1] Measured
[2] Calculated

Table 1-11. Physicochemical and (Eco)toxicological properties of Bromohydroxyacetophenone.

Common name	**Bromohydroxyacetophenone**		
			
Name	5-Bromo-2-hydroxyacetophenone		
CAS #	1450-75-5		
			Unit
Physico-chemical properties [2]	Water solubility	501	mg/l
	Log K_{ow}	2,86	
	Henry's law constant	0,052	$Pa*m^3/mol$
	Vapour pressure	0,041	Pa
Ecotoxicology aquatic [2]	EC_{50}	3,66	mg/l
	$PNEC_{freshwater}$	0,07	mg/l
	$PNEC_{sed}$		mg/kg
Persistence, Bioaccumulation, Toxicity (PBT) [2]	Persistent Not bioaccumulative Toxic		
Theoretical removal in STP	4,69 %		

[1] Measured
[2] Calculated

1.4 Environmental quality standards

Environmental quality standard (EQS) for surface water according to the water framework directive (2013/39/EU) is available for nonylphenol (including isomers 4-nonylphenol and 4-nonylphenol [branched]) and octylphenol (including isomer 4-[1,1',3,3'-tetramethylbutyl]-phenol), see Table 1-12.

Table 1-12. EQS values for nonylphenol and octylphenol.

Substance	**CAS**	**AA-EQS Inland surface waters**	**MAC-EQS Inland surface waters**
Nonylphenol	84852-15-3	0,3	2,0
Octylphenol	140-66-9	0,1	n/a

2 Methods

2.1 Sampling strategy

The Swedish EPA requested that a total of 32 samples should be taken.

Sweco devised a sampling strategy based on:

1. Maximizing the possibility for detecting the substances in question in surface waters and sediments
2. The need to demonstrate that the substances occurred at elevated concentrations relative to background concentrations in the vicinity of paper recycling mills.

Samples were collected at five different paper recycling mills. The mills are all situated in the southern part of Sweden, with Hallsta bruk being the most northern sampling point (Figure 2-1, Table 2-1). Sampling points were chosen in dialogue with the Swedish EPA and the regional county boards where the paper mills are located.

To maximize the possibility for detection, composite samples were taken in sediments and water. In most cases, sediment close to the mills was characterized by erosion conditions. Samples were always taken at the closest downstream point were non-erosion sediments could be found.

At four mills one sample was taken upstream and one sample downstream. For Hallsta mill it was possible to take two samples downstream and two upstream respectively, and for Hylte mill one sample was taken upstream and three samples downstream. This was made in order to detect gradients in substance concentrations resulting from the effluents from the mills.

Figure 2-1. Geographical overview of mills included in this study. Background map © Lantmäteriet.

Table 2-1. Sampling points and the types of samples investigated for the substances in question. Also, additional test for estrogenic/androgenic activity where made with ER-/AR-CALUX tests for five sampling stations.

Paper recycling mill	Sampling station (approximate distance to mill discharge point)		Additional CALUX tests
Bråviken mill	Bråviken	Upstream (1500 m)	
		Downstream (1000 m)	X
Nyboholms mill	Emån	Upstream (1500 m)	
		Downstream (6000 m)	
Hallsta mill	Edeboviken	4 Upstream (700 m)	
		3 Upstream (150 m)	
		2 Downstream (150 m)	
		1 Downstream (1000 m)	
Fiskeby mill	Motala ström, Norrköping	Upstream (500 m)*	X
		Downstream (1500 m)*	X
Skärblacka mill	Motala ström, Skärblacka	Upstream (1000 m)	X
		Downstream (1000 m, water)	X
		Downstream (1500 m, sediment)	
Hylte mill	Nissan	1 Upstream (1000 m)	
		2 Downstream (1500 m)	
		3 Downstream (5000 m)	
		4 Downstream (9000 m)	
Total number of sample points:		**16**	**5**

*No sediment samples possible.

Figure 2-2. Sampling points at Bråviken mill.

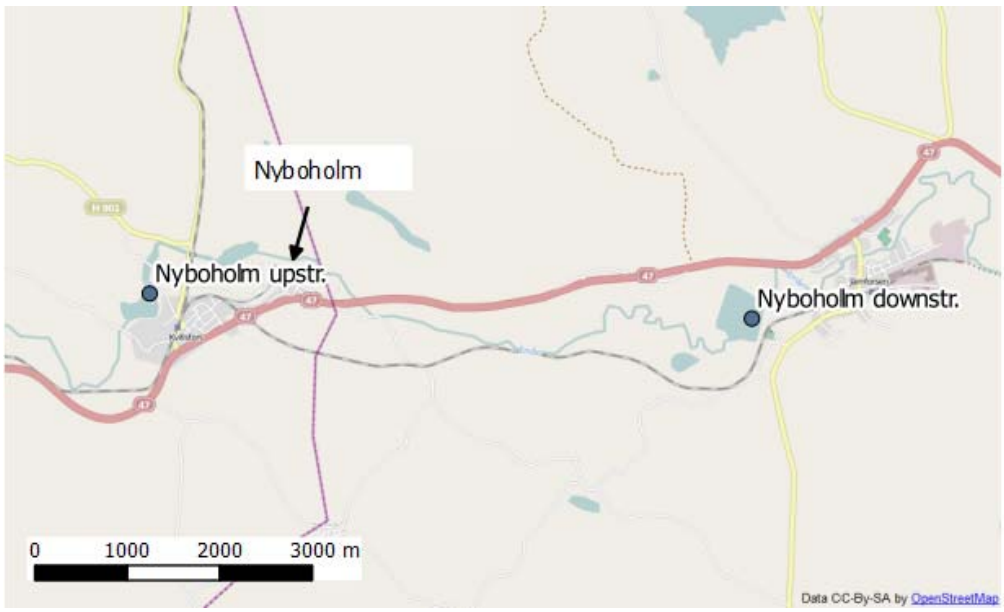


Figure 2-3. Sampling points at Nyboholm mill.

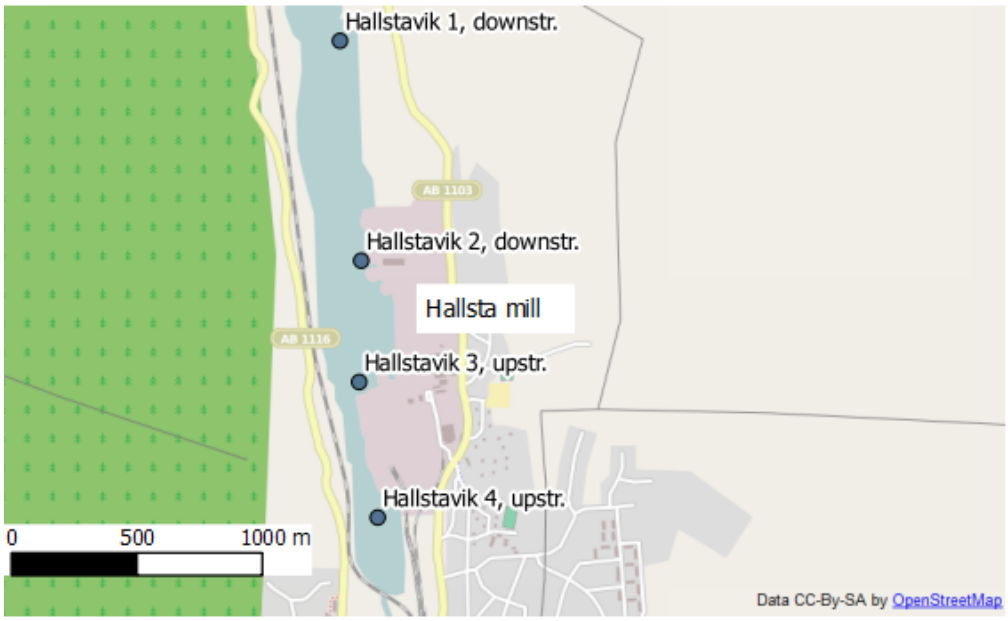


Figure 2-4. Sampling points at Hallsta mill.

Figure 2-5. Sampling points at Fiskeby mill.

Figure 2-6. Sampling points at Skärblacka mill.

Figure 2-7. Sampling points at Hylte mill.

2.2 Sampling methods

Sampling instructions were given to all sampling personnel. The instructions included sampling procedures and handling of samples during transport.

2.2.1 Sediment

Sediment samples were collected by means of a core sampler from the topmost layer (0-5 cm). Several samples were taken within a few meters interval at the sampling point and mixed to a composite sample up to the amount needed by the laboratories.

All sediment samples were transferred to pre-burned and dark glass jars and sent to laboratory within one or two days of collection. They were stored cold until analysis.

2.2.2 Surface water

Unfiltrated water was collected in clean in acid rinsed pre-burned dark glass bottles. The bottles were filled to one third three times (resulting in a filled bottled) within a few meters interval at the sampling point. Water samples were stored cold until analysis.

2.3 Analytical methods

2.3.1 Chemical analysis

Analytical methods and limits of quantification (LOQ) for the substances are shown in Table 2-2.

Table 2-2. Analytical methods for and levels of quantification (LOQ) in water and sediment.

Substance	Extraction and preparation	Method of analysis	Accredited analysis	LOQ Water (µg/l)	LOQ Sediment (µg/kg dw)
4NP: 4-Nonylfenol (branched)	Water: Steam destillation used on 0.2 L samples. Sediment: Liquid-liquid extraction followed by solid-phase extraction and clean-up of 2-10 g samples. Analytes were derivatized and quantified using internal standards (labelled analytes).	GC/MS	yes	0,1	20
4NPEO1: 4-Nonylfenol (branched)-1-etoxylat		GC/MS	yes	0,1	20
4NPEO2 : 4-Nonylfenol (branched)-2-etoxylat		GC/MS	yes	0,1	20
4tOP : 4-tert-Oktylfenol		GC/MS	yes	0,01	10
4tOPEO1: 4-tert-Oktylfenol-1-etoxylat		GC/MS	yes	0,1	20
4tOPEO2: 4-tert-Oktylfenol-2-etoxylat		GC/MS	yes	0,1	20
C10-14 Monoalkylbenzene sulfonic acid, sodium salt	Sediment: 2,5g samples were extracted with 40 ml methanol/water (1/1), freezed and centrifuged.	LC-MS/MS	yes	100	10 000
Bisfenol-A	Liquid-liquid extraction with hexane followed by derivatization	GC-MS	yes	0,05	10
1,2- Bis(3-metylfenoxy)etan	Liquid-liquid extraction with hexane	GC-MS	Internal validation	0,01	10
1,1′-Ditolyletan		GC-MS	Internal validation	0,01	10
4,4'-Ditolylmetan		GC-MS	Internal validation	0,01	10
2,6-Di isopropylnaftalen		GC-MS	Internal validation	0,01	10
BNM: Bromonitrometan	Head-space analysis	GC-ECD	Internal validation	0,1	100
Bromohydroxyacetophenone*	Solid phase extraction followed by liquid extraction and drivatization.	GC-MS	Internal validation	0,01	50

*Only analysed in sediments

2.3.2 Ecotoxicological measurements

Water and sediment samples were sent to Alcontrol for evaluation of acute ecotoxicological effects using the Microtox® test system.

The procedure employs the bioluminescent marine bacterium (Vibrio fischeri) as a test organism. The bacteria are exposed to a range of dilutions of the matrix (water and sediment) being tested. The reduction in intensity of light emitted from the

bacteria is measured along with standard solutions and control samples. The change in light output (bioluminescence) and concentration of the tested material produce a dose / response relationship. The results are normalized and the EC50 (concentration/dilution producing a 50% reduction in light) is calculated.

Microtox® tests were performed according to the standard ISO 11348-3, 1998.

2.3.3 Estrogenic and androgenic effects

The presence of estrogenic substances in water was evaluated with a cell based test system; ”Estrogenic Responsive - Chemically Activated Luciferase eXpression” (ER-CALUX).

After sample collection, a simple extraction method is used to extract the chemical content. The extract is cleaned-up and fractionated if desired, after which the clean extract is dissolved in DMSO. Meanwhile, BDS' CALUX® cells are cultured and finally grown in 96-well plates under standardized conditions. Once a confluent monolayer is obtained, the cells are exposed to the diluted cleaned extracts. After lysation and adding luciferin, the luciferase activity is quantitated using a luminometer.

Detected luminescense from the analysed samples is compared to the detected luminescense from a standard curve and is reported as estrogen equivalents (ng 17-β-estradiol eq./liter).

Androgenic substances was evaluated by “Androgen Responsive - Chemically Activated Luciferase eXpression” (AR-CALUX)”, using the same principle as ER-CALUX but a different cell culture with androgen receptors. The results is presented as equivalents of the dihydrotestosteron standard (ng Dihydrotestosterone eq./l water).

The CALUX tests has been performed by BioDetection Systems, The Netherlands.

3 Results

3.1 Concentration of substances

The results are summarized in Table 3-1. No substances occurred at concentration >LOQ apart for Bisphenol-A in sediments adjacent to the Hallsta paper mill (Table 3-2).

The highest concentration of Bisphenol-A occurred at the closest point downstream Hallstavik mill. It should be noted that the production of recycled paper at Hallsta mill has been discontinued. Substances related to these activities consequently are consequently indicators of historical activities.

Table 3-1. Number of samples with levels above LOQ for the analyzed substances.

Paper recycling mill	Sampling station		Number of substances with levels >LOQ	
			sediment	water
Braviken mill	Bråviken	Downstream (1500 m)	0	0
		Downstream (1000 m)	0	0
Nyboholms mill	Emån	Upstream (1500 m)	0	0
		Downstream (6000 m)	0	0
Hallsta mill	Edeboviken	4 Upstream (700 m)	0	0
		3 Upstream (150 m)	1 (Bisphenol-A)	0
		2 Downstream (150 m)	1 (Bisphenol-A)	0
		1 Downstream (1000 m)	1 (Bisphenol-A)	0
Fiskeby mill	Motala ström, Norrköping	Upstream (500 m)*	0	0
		Downstream (1500 m)*	0	0
Skärblacka mill	Motala ström, Skärblacka	Upstream (1000 m)	0	0
		Downstream (1000 m)	0	0
		Downstream (1500 m)		
Hylte mill	Nissan	1 Upstream (1000 m)	0	0
		2 Downstream (1500 m)	0	0
		3 Downstream (5000 m)	0	0
		4 Downstream (9000 m)	0	0

* No sediment samples possible

Table 3-2. Levels of Bisphenol-A in sediments at Hallsta mill LOQ.

Sample station	Bisphenol-A (µg/kg dw)	Matrix
Hallsta mill, Edeboviken 3, approx. 1000 m upstream	<10	Sediment
Hallsta mill, Edeboviken 3, approx. 150 m upstream	12	Sediment
Hallsta mill Edeboviken 2, approx. 150 m downstream	20	Sediment
Hallsta mill Edeboviken 1, approx. 1000 m downstream	11	Sediment

3.1.1 Comparison with PNEC and EQS

The European Commission has conducted an environmental risk assessment of Bisphenol-A including a review of measured concentrations in freshwater and freshwater sediments within the EU (Table 3-3).

Table 3-3. A comparison between measured levels of Bisphenol A in freshwater sediments in the EU (EC 2008), measured levels at Hallsta paper recycling mill and predicted no effect concentration (PNEC).

Measured levels in EU	Measured levels Hallsta mill	PNEC
Median: 16 µg/kg dw 5-95 percentile: 0,5-256 µg/kg dw	11-20 µg/kg dw	63 µg/kg dw

There are indications of a concentration gradient in sediment samples with higher levels of Bisphenol A closer to the Hallstavik mill and lower levels at longer distances from the Hallstavik mill. There is also a noticeable difference between upstream and downstream levels. The levels 1000 m downstream are similar to the levels 150 m upstream, both concentrations being similar to the median value for Bisphenol-A in sediments in the EU (see Table 3-3). No ecotoxicological effects are expected at these levels since the PNEC is considerably higher (63 µg/kg dw).

A comparison between PNECs, AA-EQS and measured concentrations (Bisphenol-A) or LOQ is made in Table 3-4. Experimental data for the toxicity is scarce for these substances, and mostly a PNEC was derived by QSAR estimation from EPI Suite[3], thus with a higher degree of uncertainty compared to experimental values. EPI Suite gives a value for chronic toxicity which is a interpolation between simulated LOEC (lowest effect concentration) and NOEC (no observed effect concentration). PNEC was calculated using an assessment factor of 10, thus dividing the lowest chronic toxicity value by 10.

All measured concentrations or LOQs are well below PNEC and thus no direct toxic effect is expected from these substances in freshwater adjacent to paper recycling mills.

[3] EPI Suite is a free software that is made available by the US EPA (www.epa.gov). It uses quantitative structure-activity relationships (QSARs) to model properties of chemical substances.

Table 3-4. A comparison between PNEC, AA-EQS and measured concentration or LOQ for the substances analysed in this study.

Substance	Matrices Water (µg/l) Sediment (µg/kg dw)	Measured concentration or LOQ	PNEC	AA-EQS inland surface waters
4NP: 4-Nonylfenol (branched)	Water: Sediment:	<0,1 (LOQ) <20 (LOQ)	0,614 4620	0,3
4tOP : 4-tert-Oktylfenol	Water:	<0,01		0,1
C10-14 Monoalkylbenzene sulfonic acid, sodium salt	Water: Sediment:	<100 (LOQ) <10 000 (LOQ)	270 23 800	
Bisphenol-A	Water: Sediment:	<0,05 (LOQ) 11-20	1,6 63	
1,2-bis(3-methylphenoxy)ethane	Water:	<0,01 (LOQ)	0,066 *	
meso-2,3-Diphenylbutane	Water:	<0,01 (LOQ)	$1,5*10^{-3}$ *	
Di-p-tolylmethane	Water:	<0,01 (LOQ)	$3,6*10^{-3}$ *	
2,6-Diisopropylnaphthalene	Water:	<0,01 (LOQ)	$0,2*10^{-3}$ *	
BNM: Bromonitromethane (degradation product from bronopol)	Water:	<0,1 (LOQ)	11,6 *	
5-brom-2-hydroxyacetophenon	Water:	<0,01 (LOQ)	0,07 *	

*calculated

3.2 Ecotoxicological effects

No measureable ecotoxicological effect could be found with the Microtox method with the exception of a weak initial effect in one sample station (upstream Hyltebruk, Table 3-5).

Table 3-5. Microtox testing results for the sample station upstream Hyltebruk. A higher value indicates lower toxicity.

Exposure time (min)	EC_{50} (%)	EC_{20} (%)
5	>82	81
15	>82	>82
30	>82	>82

3.3 Estrogenic/androgenic activity

The levels of endocrine disruptive activity are presented in Table 3-6. The levels of estrogenic and androgenic activity are similar in all samples.

Androgenic effects were detected downstream the Bråviken and Skärblacka mills but at levels below LOQ. Consequently they are reported as detected. There is a weak indication of androgenic impact at two of the paper mills, but given the very similar results this may indicate a background androgenic signal.

Estrogenic effects were detected at all sampling points except for downstream Skärblacka, although only at quantifiable levels upstream Skärblacka. There is an indication of higher levels upstream the mills, thus indicating a different source than the paper recycling mill.

Table 3-6. Results from analysis of estrogenic and androgenic activity in surface water. Detectable levels below LOQ but above LOD is an approximation (~). Non-detectable results followed by (LOD).

Paper recycling mill	Sampling station		AR-CALUX Androgens (ng Dihydrotestosterone eq./l)	ER-CALUX Estrogens (ng 17ß-estradiol eq./l)
Bråviken	Bråviken	downstream	detected (~0,46)	detected (~0,06)
Fiskeby	Motala ström, Norrköping	upstream	not detected (<0,25)	detected (~0,07)
		downstream	not detected (<0,25)	detected (~0,04)
Skärblacka	Motala ström, Skärblacka	upstream	not detected (<0,25)	detected 0,065
		downstream	detected (~0,25)	not detected (<0,04)

4 Discussion

4.1 Previous measurements in Sweden

Data from earlier screening studies (www.ivl.se) in Sweden have shown concentrations of Bisphenol A in sediments between 1 and 60 µg/kg dw, although the majority of measurements have been below LOQ (<50 µg/kg). In surface water concentrations ranging from 0,006 to 0,12 µg/l have been found but the median value is below LOQ (<0,005 µg/l) Consequently Bisphenol A is not expected to be found in most surface waters, but may be found at low concentrations in sediments.

Similarly, nonylphenol has been measured in Sweden at concentrations of 7,3-15000 µg/kg dw (median <10 µg/kg) in sediments and 0,01-0,15 µg/l (median <0,01 µg/l) in surface waters.

In a screening study from 2008 (IVL), LAS (C10-C14) substances was not found in surface waters or sediments from background areas, but was measured at concentrations between 270 and 1600 µg/kg dw (median 295 µg/kg) in sediments, and between 0,0021 and 83 µg/l (median 3 µg/l) in surface water near urban or industrial areas.

In comparison, the levels below LOQ seen for nonylphenol and LAS in this study indicates background levels rather than surface waters being impacted by point sources. Levels of Bisphenol A close to Hallsta Mill indicates regionally or locally elevated background levels (since upstream concentrations approx. equal to further downstream) and/or the presence of a new or old point source (possibly Hallsta bruk).

4.2 Substances in surface water systems at other paper recycling mills

The substances related to thermal paper (receipts etc.)[4] studied in this report have been found in the vicinity of paper recycling mills in Japan at levels between 10-1600 µg/l water and 2,2-190 µg/kg sediment (Terasaki et al 2008). However these levels were measured in an area with 85 pulp and paper mill and recycling paper mill industries. This cannot be compared to the situation at the paper mills of the present study where the mills occured alone.

In another study eight phenolics were detected in samples collected from areas where paper-recycling process water is discharged (Terasaki et al 2007)). The

[4] 1,2-bis(3-methylphenoxy)ethane, meso-2,3-Diphenylbutane, 4,4'-Ditolylmetan, 2,6-Diisopropylnaphthalene

phenolics[5] occurred at concentrations up to 270 µg/l in outfall water and 230 000 µg/kg in sediment samples collected from outfall areas. The estrogenic activities of the phenolic compounds were assessed using YES assays, showing that they exhibited weak – strong estrogenic potency. This study was also performed in an area where a multitude of pulp and paper mill and recycling paper mill industries affect a limited surface water system and hence, the findings in the sediments cannot be compared to the areas investigated in the present study. However, this study demonstrated the value of investigating outfall water from the paper mills as a 1st tier step in an effort to understand the impact of these industries on the aquatic environment.

4.3 Removal in WWTPs

According to experimental results a high degree of removal in the internal waste water treatment plants is expected for Bisphenol A, especially for plants with a de-inking step (EC 2008). Also, Bisphenol A would appear to be readily biodegradable, possibly requiring a short period of adaptation (EC, 2003). The theoretically calculated removal rates in sewage treatment plants are relatively high for several of the other substances (section 1.3.2). For Bromonitromethane and Bromohydroxyacetophenone the STP removal rate is estimated to be low and is not a likely cause for the low concentrations in the environment.

4.4 Conclusions and recommendations

The reasons for the lack of occurrence of the investigated substances downstream paper recycling mills may be:

- Only surface water recipients with few or single sources were studied indicating that the total load is not sufficient to detect these substances in the environment
- There are calculations and/or measurement (section 4.3) showing that many of the substances may be removed to a high degree in the waste water treatment of the paper mills.
- Seasonal or other time related variations decrease the possibility of finding these substances in grab samples of surface water. However, sediment sampling should not be affected by temporal variation.
- The particular substances might be replaced (in whole or partly) by other equivalent substances in the paper-recycling industry. There are sugar- and protein-based surfactants as viable alternatives to petroleum based ones (Vendetti et al.), and also a broad range of biocides that can be used in the in the paper recycling process.

[5] e.g. totarol, 2,4-bis(1-phenylethyl)phenol, 4,4'-butylidenebis(6-t-butyl-m-cresol), 2,4-bis(1-phenylethyl)-6-chlorophenol and 4-hydroxy-4'-isopropoxydiphenyl sulfone

According to the Swedish Chemicals Agency, the usage of Bispehonl A in pigment/dye related products was 17 tonnes in 2011. 140 tonnes of nonylphenol was registered in Sweden 2011. It is unclear how much of this usage is related to recycled paper, and no conclusions based on usage in Sweden can be drawn.

The overall conclusions are that recycled paper mills do cause noticeably increased concentrations of the investigated substances in the downstream surface water environment. A comparison between LOQ/measured concentrations and PNEC values show that the water environment is probably not negatively affected by emission of these substances from recycling paper mills. It is unknown to what degree other substances from recycling paper mills impact the aquatic environment.

No further measurement of the investigated substances downstream of the recycling peppermills is necessary.

If the impact of this industry sector on the aquatic environment is to be further investigated, the following steps are recommended:

1. In cooperation with the industry and e.g. the Swedish Chemicals Agency, identify possible substances that are being used at present in the industrial processes
2. Identify which of the substances from step 1 that are most likely not to be reduced in the industrial WWTPs
3. As a first screenings study, measure substances from step 2 only in effluents from the industrial WWTPs
4. Use the results from step 3 as a basis for measurements in receiving surface waters. Choose measurement matrixes (water, passive samplers, sediment, fish) based on the properties of the substances to be investigated

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