

Content

Preface.....	7
Summary	9
Sammanfattning.....	11
1. Frame of the study	13
2. Background	15
2.1 Bronopol; Chemical properties, fate and toxicity.....	15
2.2 m-Cresol; chemical properties fate and toxicity	16
2.3 Resorcinol; chemical properties, fate and toxicity.....	16
2.4 Triclosan; chemical properties, fate and toxicity.....	17
2.5 Summary of estimated PNECs	18
3. Application, use and previous measurements	19
3.1 Application and use.....	19
3.2 Environmental levels and exposure	22
4. Methodology	25
4.1 Sample selection.....	25
4.1.1. Denmark.....	25
4.1.2. Faroe Islands	25
4.1.3. Finland	26
4.1.4.Iceland.....	27
4.1.5. Norway.....	27
4.1.6. Sweden.....	28
4.2. Sampling	31
4.3Chemical analysis of the collected samples.....	32
4.3.1 Analysis of water samples.....	32
4.3.2 Analysis of biota samples.....	32
4.3.3 Analysis of sludge, sediment and soil samples.....	33
4.3.4 Analysis of Air.....	33
4.3.5 Derivatisation	33
4.3.6 Silica gel column.....	34
4.3.7 GC/MS quantification of IVL- samples	34
4.3.8 HPLC/HRMS quantification of NILU- samples	34
4.4 Quality control and method comparison.....	35
4.4.1 Recoveries.....	35
4.4.2 Limit of detection.....	36
4.4.3 Identification	36
4.4.4 Laboratory and field blanks.....	36
4.4.5 Bronopol stability test	36
4.4.5 Laboratory intercomparison	38
5. Results and discussion	39
5.1 Concentrations in samples from STPs and landfills	39
5.1.1 Sewage water from municipal STPs.....	39
5.1.2 Industrial STPs.....	41
5.1.2 Sludge	41
5.1.3 Leachate water	43
5.2 Environmental concentrations.....	44
5.2.1 Air	44
5.2.2 Surface water.....	44
5.2.3 Sediment and soil.....	44
5.2.4 Biota.....	46

5.3 Concentration patterns at geographically related sites	46
5.4 Ecotoxicological risk assessment	47
6. Summary and conclusions.....	49
7. Acknowledgements	51
References.....	53
Appendix 1; Sample characteristics	57
Appendix 2. Sampling Manual.....	67
Appendix 3; Result table.....	73

Preface

Since 2001 the Nordic countries have systematically been screening the environment for potentially hazardous substances. The aim of the Nordic environmental screening of substances is to obtain a snapshot of the occurrence of potentially hazardous substances in the environment both in regions most likely to be polluted as well as in some background areas. The focus is on little known, anthropogenic substances and their derivatives, which are either used in high volumes or are likely to be persistent and hazardous to humans and other organisms. The substances of focus in this study, bronopol and resorcinol, are included due to their toxicity and volume, and not because they are very persistent or bioaccumulating. This was done to gain experience in environmental screening of this kind of substances. If the substances subjected for screening are found in significant amounts this may result in further investigations or monitoring on national level.

The Nordic screening project is run by a project group with representatives from the National Environmental Research Institute of Denmark, the Finnish Environment Institute, the Environment and Food Agency of Iceland, the Food-, Veterinary and Environmental Agency of the Faroe Islands, the Norwegian Pollution Control Authority and the Swedish Environmental Protection Agency. The selection of the substances was made by the project group.

The project is financed and supported by the Nordic Council of Ministers through the Nordic Chemicals Group and the Nordic Monitoring and Data Group as well as the participating institutions. The chemical analyses have been carried out jointly by the Norwegian Institute for Air Research (NILU) and the Swedish Environmental Research Institute (IVL).

The respective participating Nordic countries organised sample selection and collection and transport of samples based on a sample protocol and manuals provided by the analytical laboratories.

Summary

The aim of this screening programme was to investigate the occurrence of bronopol and resorcinol in environmental samples from the Nordic countries. In order to allow for some comparisons two other chemicals, *m-cresol* and triclosan, both with known environmental distribution and earlier subjected to screening, were added to the programme.

The compounds selected for this screening are widely used. Because of their application they may end up in the environment through various waste streams. In the screening the concentrations of the chemicals were determined in a variety of media, collected at different geographical sites and representing different source characteristics e.g. point sources and dispersed use related to many activities and products. An additional aim was to highlight important transport pathways and to estimate current emissions.

Despite a high consumption of *bronopol* in the Nordic countries as well as in the EU, it was not found in any of the samples analyzed. Bronopol undergoes rapid hydrolysis as well as biodegradation, which may explain its absence in the environmental matrix samples.

Resorcinol is widely used and was also frequently found in the municipal influent water samples. Despite that it is significantly reduced in the Sewage Treatment Plants (STPs) along with a reported high biodegradability, it is still present in some effluent water samples. More importantly it was also detected in environmental samples of water and sediment. Concentrations of resorcinol are higher than the concentration of triclosan in environmental samples outside point sources but are lower or in the same range as triclosan in environmental samples outside municipal STPs. In contrast to triclosan resorcinol seem to be more present in water samples than in sediment samples.

Triclosan was found in high concentrations in STP sludge. This may be a reflection of the use of triclosan in health care products. Triclosan was also frequently detected in STP effluent water and in sediment outside STPs. The present study shows that, despite a stated decreased usage of the compound within the industry, triclosan is still detected in and around STPs and in some environmental samples.

The registered usage volume of *m-cresol* is only available for Sweden, however, the compound was found in several influent and effluent samples from municipal STPs in Denmark, Finland and Sweden and in leachate water samples in Finland and Sweden. In effluent water and in environmental samples it was however mainly found in the vicinity of an industrial pulp and paper STP in Finland. Earlier studies have shown the importance of emissions from biomass burning for this compound and

this along with the diffuse spreading of the substance from products not registered in SPIN seem to be of importance for municipal and industrial STP concentrations. A high removal efficiency of the substance seems however to limit its environmental distribution.

Sammanfattning

Målsättningen med denna screening har varit att undersöka förekomst av bronopol och resorcinol i miljöprover från de nordiska länderna. För att möjliggöra jämförelse med andra ämnen har även två referenssubstanser, m-cresol och triclosan, med tidigare känd förekomst och fördelning i miljön inkluderats i studien.

De ingående ämnena har stor användning inom flera olika områden och kan därför nå miljön via flera olika vägar. Ämnena har därför analyserats i flera i olika matriser. Prover har dessutom valts ut med syfte att få en geografisk spridning samt för att representera olika typer av spridningskällor t.ex. punktkällor respektive diffus användning relaterad till produkter.

Trots en hög konsumtion av *bronopol* så väl i de nordiska länderna som inom EU, kunde ämnet inte detekteras i något av de analyserade proverna. Bronopol hydrolyseras snabbt samt har en snabb nedbrytningsprocess vilket kan förklara varför man inte kan återfinna ämnet i miljön.

Resorcinol används brett och detekterades också frekvent i det inkommande vattnet till reningsverken. Trots att det reduceras avsevärt under reningsverksprocesserna och trots att ämnet har en hög nedbrytningspotential går det fortfarande att återfinna resorcinol i utgående vatten från reningsverken och i vissa ytvatten och sedimentprover. Koncentrationen av resorcinol var högre än triclosan utanför vissa punktkällor men lägre eller i samma nivå i miljöprover utanför reningsverk. Till skillnad från triclosan förekommer resorcinol oftare i vattenprover än i sedimentprover.

Triclosan detekterades i höga koncentrationer i reningsverksslam. Triclosan återfanns också frekvent i utgående vatten från och i sedimentprover utanför reningsverk. Föreliggande studie visar att det trots en påstådd minskad användning av industrin kan triclosan fortfarande detekteras i reningsverksprover och i miljön.

Registrerade användningsvolumer för *m-cresol* finns bara för Sverige, trots detta kunde ämnet detekteras i flera inkommande vattenprover till reningsverk i Danmark, Finland och Sverige. I utgående vatten och i miljöprover återfanns det däremot enbart i närheten av en papersmassfabrik i Finland. Tidigare studier av emissioner från förbränning av biomassa har påvisat denna källas betydelse för halter av m-cresol i miljön. Detta tillsammans med diffus spridning från produkter som inte registreras i spin-databasen tycks vara av stor betydelse för detta ämne avseende reningsverkshalterna. En hög reningseffekt i reningsverken tycks däremot begränsa dess spridning i miljön.

1. Frame of the study

The aim of this screening programme was to investigate the occurrence of bronopol and resorcinol in environmental samples from the Nordic countries. In order to allow for some comparisons two other chemicals, m-cresol and triclosan, both with known environmental occurrence and distribution and earlier subjected to screening, were added to the programme.

The compounds selected for this study are widely used chemicals. Because of their application they may end up in the environment through various waste streams. In the screening, the concentrations of the chemicals were determined in a variety of media, collected at different geographical sites and representing different source characteristics e.g. point sources and dispersed use related to many activities and products. Background samples were also taken. An additional aim was to highlight important transport pathways and to estimate current emissions.

The results of this screening project will be part of scientific measures to estimate the environmental risk posed by these chemicals in the vulnerable Nordic ecosystems.

The structures of the chemicals are shown in Figure 1–4.

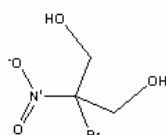


Figure 1. Bronopol
(2-Bromo-2-nitropropane-1,3-diol, CAS 52-51-7)

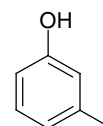


Figure 2. m-Cresol
(3-methylphenol, CAS 108-39-4)

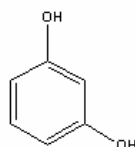


Figure 3. Resorcinol
(1,3-Benzenediol, CAS 108-46-3)

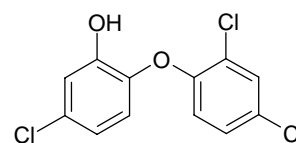


Figure 4. Triclosan
(2-Hydroxy-2',4,4'-trichlorodiphenylether CAS 3380-34-5)

2. Background

2.1 Bronopol; Chemical properties, fate and toxicity

Bronopol (2-bromo-2-nitropropane-1,3-diol, CAS 52-51-7) forms white to slightly yellow crystals. Due to its application in many consumer available products, bronopol is released to the environment through various waste streams (see below). The substance is highly soluble in water and not expected to bioaccumulate. Literature references on the issue of the persistence of bronopol are ambiguous. Some state that it is stable to hydrolysis under normal conditions but at increased temperatures and/or higher pH rapid hydrolysis may occur (EPA, 2006 a). Others state that in aqueous solution bronopol is easily transformed to formaldehyde. Other transformation products consist of bromonitroethane, bromoethanol, and bromonitroethanol (Wang, 2002).

When released to water bronopol is not expected to adsorb to suspended solids and sediments nor is vaporisation from the water phase expected to be an important transport pathway (HSDB, 2006). Bronopol is easily biodegradable (EPA, 2006).

Table 1. Chemical and physical data

Substance	MW (g/mol)	W_{sol} (g/l)	V_p	H (Atm m ³ /mol)	Log K_{ow}	BCF (L/kg)	K_{oc}	Ref
Bronopol	199.9		$1.3 \cdot 10^{-5}$ mmHg (25°)	$1.3 \cdot 10^{-11}$			5	1
m-Cresol	108.1	22.7 (25°)	0.11 mm Hg (25°)	$8.56 \cdot 10^{-7}$ (25°)	1.96			2
Resorcinol	110.1	1400 (20°)	$2.7 \cdot 10^{-4}$ hPa (25°)	$8.1 \cdot 10^{-11}$ (25°)	0.8-0.97	2.4	65	3
Triclosan	289.6	0.012	$7 \cdot 10^{-4}$		4.8			4

Ref 1: HSDB, 2006; 2: SRC 2006; 3: ESIS, 2006; 4: Samsö-Petersen et al, 2003

When released to air, the vapour pressure indicates that bronopol may exist both in the particulate phase and in the vapour phase where it may react with hydroxyl radicals with an estimated half-life of 97 hours (HSDB, 2006).

For ecological risks, bronopol is practically non-toxic to slightly toxic to birds; slightly to moderately toxic to freshwater fish and terrestrial invertebrates; moderately to highly toxic to estuarine/marine invertebrates; and slightly toxic to estuarine/marine fish (EPA, 2006). Bronopol is classified as harmful if swallowed or in contact with skin; irritating to eyes, respiratory system and skin; risk of serious damage to eyes and very toxic to aquatic organisms (Xn; R21/22 - Xi; R37/38-41 - N; R50; ESIS, 2006).

