

HAZARDOUS SUBSTANCE OCCURRENCE IN BALTIC SEA PILOT MUNICIPALITIES

MAJOR OUTPUT FROM THE TRACKING AND RANKING
FOR PRIORITISATION OF SOURCES IN NONHAZCITY
PROJECT

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CONTENTS

1 Introduction	4
1.1 The NonHazCity Project	4
1.2 Hazardous substances – how are they defined? What are they?	4
1.3 Sources of hazardous substances in urban areas	5
1.4 Policy settings	5
2 Screening activities in pilot cities.....	7
2.1 Selection of sampling points.....	7
2.2 Sample collection and delivery to analytical laboratories	8
2.3 Methodological descriptions of hazardous substances analysis	8
3 Results and discussion of hazardous substance screening in municipalities	10
3.1 Metals.....	10
3.2 Phthalates	12
3.3 Alkylphenols	16
3.4 Bisphenol A	19
3.5 Perfluoralkyl Substances (PFAS)	20
3.6 Pharmaceuticals.....	24
3.7 Local priority substances.....	27
4 Source Mapping of Local Priority Hazardous Substances	28
4.1 Method	28
4.2 Local Substance Source Maps.....	29
5 Hazardous substances in articles and materials.....	33
6 Summary and recommendations	36
7 References	38

1 INTRODUCTION

1.1 The NonHazCity Project

The assessment of the status of the Baltic Sea environment by HELCOM (Baltic Marine Environment Protection Commission - Helsinki Commission) has shown that the load of hazardous substances to the marine environment is an issue of major concern. Despite a number of regulations and other measures for emissions reduction, hazardous substances (HS) are still released from land-based sources to the aquatic environment. These releases occur through three main pathways: industrial and municipal wastewaters, and stormwater. While emissions of some hazardous substances from major industrial sources are regulated by permits of operation and both municipal and industrial discharges are treated in wastewater treatment plants (WWTPs), other control measures at the source are needed to efficiently reduce emissions from the vast number of small scale emitters in urban areas.

The Interreg Baltic Sea Region Project NonHazCity (“Innovative management solutions for minimizing emissions of hazardous substances from urban areas in the Baltic Sea Region”) aims to demonstrate possibilities for municipalities and WWTPs to reduce emissions of priority hazardous substances and other pollutants from small scale emitters in urban areas that cannot be controlled by traditional water treatment and enforcement techniques. Target substances of concern will be identified and prioritized, sources tracked and ranked; and individual Hazardous Substance Source Maps and Chemicals Action Plans will be developed by each partner municipality.

The NonHazCity consortium of partners and associates consists of a group of 9 municipalities and expert organisations from the Baltic Sea Region (BSR) that have taken responsibility to find new ways to tackle the large number of emissions of hazardous substances from very small and scattered sources in their urban territories.

The present report is a summary of the results obtained during the substance screening and the source tracking performed in the NonHazCity project. The overall aim was to find out where project target substances occur in the urban sewer systems of partner municipalities and to **track back their potential sources. For this purpose, a pilot screening of hazardous substances** in wastewater streams (e.g. residential, stormwater, etc.) has been performed. Source maps for selected hazardous substances were established. In addition, the municipality of Stockholm performed a pilot study of hazardous substances in indoor used articles and materials.

1.2 Hazardous substances – how are they defined? What are they?

Substances are usually regarded as hazardous if they are harmful to the health of organisms and/or ecosystems. Certain criteria related to persistence, bioaccumulation and toxicity (PBT) must apply in order to classify a substance as hazardous. Some substances are hazardous because of their persistence and their ability to accumulate in organisms to levels causing harmful effects. Other substances are classed as hazardous due to their toxic properties. Some persistent and bioaccumulative substances may travel long distances thereby polluting not just areas near their emission sources but potentially around the world. Endocrine disrupting compounds (EDC) are a heterogeneous group of hazardous substances with carcinogenic, mutagenic and reprotoxic (CMR) properties. The list of known EDCs includes e.g. metals such as cadmium, certain plastic additives and synthetic hormones, which may or may not have PBT properties. EDCs disturb the hormone system of organisms, which might cause e.g. an impairment of reproductive functions, developmental abnormalities, and obesity and negatively affect the immune system.

In the European chemicals legislation, substances might be listed as Substances of very High Concern (SVHC) if they have been classified as persistent, bioaccumulative and toxic chemicals (PBT substances) or very persistent and very bioaccumulative (vPvB), the same criteria are used within HELCOM (EU, 2011). In addition, CMR-classified substances, sometimes including EDCs which are known or suspected to be toxic for reproduction (R) or if they cause an equivalent concern as CMR or PBT/vPvB substances, are identified as SVHC. (See section 1.4 on Policy Settings, below).

1.3 Sources of hazardous substances in urban areas

The widespread occurrence of hazardous substances in the environment has raised increasing societal concern. Hazardous substances including pharmaceuticals, components of personal care products, steroid hormones, surfactants and industrial chemicals have been associated with a number of negative effects, including reproductive and endocrine disrupting effects and cancer in humans and wildlife.

The major types of urban wastewater that deliver hazardous substances to the aquatic environment via WWTPs include domestic wastewater, hospital effluents, industrial wastewater and stormwater run-off. By using consumer products and other everyday items, households emit metals and organic pollutants including phthalates, alkylphenols, pharmaceuticals and highly fluorinated substances to municipal wastewater. Households can emit hazardous substances via black water from toilets or greywater from washing, showering, floor-wiping and laundry.

Stormwater is a significant medium of urban hazardous substance transport. Pollutants emitted from e.g. buildings, vehicles and transportation infrastructure. Pollutants settled on urban surface areas may be washed off by stormwater and spilled into sewer systems or enter receiving waters directly. Stormwater runoff contains different kinds of pollutants depending on the type of urban surface on which precipitation falls.

As a consequence of the load of hazardous substances from the urban sewer system, WWTPs are significant emitters of hazardous substances to receiving waters. This is because WWTPs are not specifically designed to eliminate most hazardous substances. Hazardous substances not degraded in WWTP are either emitted to receiving surface waters or remain in the sewage sludge. Hence, sludge when used e.g. for agricultural or other purposes is a source of release of hazardous substances to the environment.

Since WWTPs cannot treat all hazardous substances emitted from numerous urban sources to the sewage system, it is necessary to reduce the emissions at the source, i.e., households, municipal entities and small scale enterprises.

1.4 Policy settings

Due to their adverse environmental and health impacts many hazardous substances are policy regulated and their occurrence in the environment is monitored.

The overall regulatory policy framework for chemicals in the EU (including HS) includes the Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH, 2006/1907/EC) and the Regulation on classification, labelling and packaging of substances and mixtures (CLP, 2008/1272/EC). Furthermore, the CLP legislation conforms to the globally harmonized system (GHS) for classification and labelling of chemicals, in order to facilitate the transfer of knowledge concerning hazardous substances for traded chemicals on a global market. The REACH-Regulation requires the registration of all chemicals that are either produced or imported into the EU in quantities equal or greater than one tonne per year. The CLP Regulation concerns the classification, labelling and packaging of chemical substances and mixtures which are sold in the EU market. Other relevant directives include the Toy Safety Directive, Water Framework Directive, Marine Strategy Framework Directive and the Urban Wastewater Treatment Directive.

The principle regulatory options under REACH and CLP are the authorisation process (including the Candidate List of target substances), restrictions and harmonised classification. Substances of very high concern (SVHC) are listed in the Candidate List which is published by The European Chemical Agency (ECHA) in accordance with Article 59(10) of the REACH Regulation. This list includes PBT and vPvB substances as well as CMR substances in accordance with the CLP Regulation. Substances with other adverse effects on humans and the environment, like EDC can also be included in the Candidate List. The list is by no means exhaustive, the process to include substances on the list is lengthy and costly, which makes the process of including substances on the list inefficient. There are other lists, for example the Substitute It Now (SIN) list which uses the same criteria for SVHC as the candidate list but does not require the same lengthy process for inclusion. Hence the SIN-list comprises 913 substances while the Candidate list only has 181 substances (as of February 2018). The SIN-list is not connected to any legislation but several big companies use this list to be proactive. Once a substance is added to the Candidate List, REACH imposes immediate obligations on manufacturers and importers to declare the substances if present in an article. Article 33(1) of the REACH Regulation states that manufacturers and

importers of articles are required to notify their commercial customers of the presence of any Candidate List substance in their products exceeding 0.1% by weight and provide instructions on safe use of the product. For non-commercial customers they only need to provide the information once the customer makes a request, with a notification period of 45 days.

The EU Water Framework Directive (WFD) (2000/60/EC) aims to regulate the use and protection of surface water bodies and the achievement of their good environmental status. It prioritises hazardous substances of EU wide concern for the aquatic environment. The Daughter Directive on Priority Substances (2008/105/EC) sets environmental quality standards (EQS) for substances in surface waters, with a subset of priority hazardous substances of particular concern. A Directive (2013/39/EU) amending and updating the Water Framework Directive (2000/60/EC) adds new substances with EQS into the priority list and sets additional EQS for biota for some bioaccumulative chemicals which can threaten both aquatic wildlife and human health via the consumption of contaminated prey or eating contaminated food, respectively.

The main objective of the EU Marine Strategy Framework Directive (2008/56/EU) regarding hazardous substances is the reduction and prevention of emissions to the marine environment, so that there are no significant impacts to marine ecosystems, human health or legitimate uses of the sea. The assessment of hazardous substances in coastal and territorial waters follows the requirements laid down in the WFD and the use of the respective EQS.

The Baltic Sea Action Plan (BSAP) of the Helsinki Convention (Convention on the Protection of the Marine Environment of the Baltic Sea Area) aims to restore the good environmental status of the Baltic marine environment by 2021. Hazardous substances are one of the four topic areas addressed by the BSAP beside biodiversity, eutrophication and marine activities. HELCOM has set a priority list of hazardous substances to be of special concern for the Baltic marine environment. As part of the HELCOM CORESET project, some hazardous substances have been selected as core indicators for the assessment of the chemical status of the Baltic Sea. An assessment of the status of the Baltic Sea made in 2010 (using data from 1999-2007), indicated that all open sea areas were affected by hazardous substance contamination.

Table 1 shows the classes of hazardous substances selected as target substances by NonHazCity and their listing in various priority lists with relation to policy settings. The substances which were selected are considered to be priority or emerging pollutants in the water environment on a local (municipality) or macro-regional (Baltic Sea region) scale. The organic pollutants include hazardous substances for which there is a lack of environmental background data due in part to a lack of a regular monitoring in the aquatic environment.

Table 1: Listing of NonHazCity target hazardous substances (HSs) on various priority lists

NonHazCity target substance	EU WFD ¹ (prior. list)	EU WFD ² (Watch List, emerg. pollut.)	HELCOM (BSAP ³ prior. list)	HELCOM (HS listed in the set of core indicators)	REACH ⁴ (Candidate list)	Stockholm Convention ⁵
Metals	Cd, Ni, Pb	Cr, Zn	Cd	Cd, Pb	Cd and Pb compounds	-
Quality standards Phthalates	DEHP	-	-	-	DIBP, DEHP, DBP	-
Alkylphenols	NP, OP	-	NP/NPE; OP/OPE	-	NP/NPE	-
Bisphenol A (BPA)	-	BPA	-	-	BPA	-
Perfluoralkyl Substances (PFAS)	PFOS	-	PFOS, PFOA	PFOS	PFOA, PFHxS	PFOS
Pharmaceuticals	-	Diclofenac; 17 α -Ethinyl-estradiol, 17 β -Estradiol	-	Diclofenac; 17 α Ethinyl-estradiol, 17 β -Estradiol	-	-

¹ EU Water Framework Directive (WFD) (2000/60/EC). The Daughter Directive on Priority Substances (2008/105/EC) set EQS for 33 substances in surface waters. Directive 2013/39/EU is updating Directive 2000/60/EC.

² EU Water Framework Directive (WFD) (2000/60/EC). The Watch List shall provide data on the concentrations of emerging or little known hazardous substances across the EU

³ The Baltic Sea Action Plan (BSAP) of the Helsinki Convention (Convention on the Protection of the Marine Environment of the Baltic Sea Area).

⁴ New substances are listed at the Candidate List which is published by The European Chemical Agency (ECHA) in accordance with Article 59(10) of the REACH Regulation (2006/1907/EC).

⁵ Stockholm Convention on Persistent Organic Pollutants (POPs)

2 SCREENING ACTIVITIES IN PILOT CITIES

2.1 Selection of sampling points

One aim of the screening activities was to document the presence of hazardous substances and their sources within the NonHazCity partner municipalities. Sources can be divided into two types - diffuse sources (e.g. emissions from articles and materials which contain hazardous substances) and point sources (primarily emissions from industry). Many of these sources are upstream of WWTPs, thus their emissions end up in WWTPs. Furthermore, there is a wide range of possible sources, and some of them are unconfirmed or unknown. Therefore, the chemical screening campaigns started with a detailed planning of sampling activities.

The selection of sampling points was performed by specialists in municipalities in cooperation with project chemical experts, local water and sewage management companies and national authorities (Environmental Services or Environmental Boards). In most cases these were local wastewater collection points or pumping stations, where in each case it could be clearly seen what type of wastewater (from an urban catchment area) had been collected there. Sampling locations targeted included e.g. printing houses, hospitals, laundries and car washing stations, cosmetic studios and hairdressers, automobile mechanics, shopping malls, and fire training areas. The two most important types of sampling points were residential areas and WWTPs.

The number of sampling points, as well as the number of different types of wastewater samples differed among the participating municipalities. The number of samples taken are presented in **Table 2**, as well as abbreviations of sample types, which were used in this report. Because the numbers of samples taken per sample type differed between municipalities the detection frequencies of hazardous substances are not directly comparable.

Table 2: General information on wastewater sample type and numbers sampled per partner municipality

Type of samples (abbreviation)	Gdańsk (Poland)	Riga (Latvia)	Pärnu (Estonia)	Turku (Finland)	Kaunas (Lithuania)	Šilalė (Lithuania)	Total No.
wastewater from residential area (RA)	5	2	2	7	1	2	19
sewage water from industrial areas (IA)	4	0	3	3	1	1	12
small and medium-sized enterprises effluents (SME)	0	5	6	0	5	4	20
stormwater (SW)	4	4	2	4	2	2	18
WWTP water							
influent sewage water (ISW),	5	2	3	2	1	1	14
effluent sewage water (ESW)	2	2	3	0	1	1	9
sewage sludge (SS)	0	2	1	0	1	1	5
Total No. per partner	20	17	20	16	12	12	97

2.2 Sample collection and delivery to analytical laboratories

A unified sampling and analysis procedure (SOP - Standard Operating Procedure) for water and sludge sampling was elaborated by experts from the University of Gdańsk (UG) and the Swedish University of Agricultural Sciences (SLU), who were also responsible for the chemical analysis. The SOP contained information about uniform procedures for sample collection (e.g. time, type of sampler, bottles), labelling and delivering. Sampling was performed between September 2016 and January 2017 by WWTP and municipality staff. Directly after sample reception in the UG and SLU laboratories, samples were unpacked, labelled and stored frozen until chemical analysis.

2.3 Methodological descriptions of hazardous substances analysis

The list of target hazardous substances is presented in **Table 3**. While metals have a long history of analysis, some of the organic substances are considered as emerging pollutants.

Analysis of metals

The analysis of metals were performed by the University of Gdańsk. The samples (without filtration) were mineralized with 65% nitric acid and 30% hydrogen peroxide. The concentrations of copper, chromium, cadmium, nickel, lead and zinc in both wastewater and sludge were determined by atomic absorption spectrometry (AAS, spectrometer AAnalyst 400, Perkin Elmer).

Analysis of organic substances

Organic substances were determined using chromatographic methods coupled with mass spectrometry. Both solid phase extraction (SPE) (for pharmaceuticals, bisphenol A, alkylphenols and perfluoralkyl substances) and liquid-liquid extraction (LLE) (for phthalates) were used as extraction techniques. The liquid samples for phthalates analysis were not filtered. The samples for alkylphenols, bisphenol A and pharmaceuticals were filtered, then analytes were extracted from suspended particles using methanol, which finally was introduced in the water samples. The solid samples were freeze-dried, extracted using solid liquid extraction, then extracts were analysed by methods presented in **Table 3**. The analytical protocols for PFAS analysis can be found in Ahrens et al. (2009, 2015), while the protocol for phthalates is from Viecelli et al. (2011). The methodology for alkylphenols, phthalates, bisphenol A and pharmaceuticals was developed specifically for the current project. The reason for the new protocol development was to analyse alkylphenols, bisphenol A and pharmaceuticals in one analytical run in both liquid and solid phases of water samples. All methods were validated using a standard protocol.

Table 3: Target hazardous substances with corresponding acronyms, analytical method and method detection limit (MDL)

Analytes	Acronym	CAS	Analytical method	MDL (water samples)	Analysis laboratory
Metals					
Copper	Cu	7440-50-8	AAS	0.001 mg/L	UG
Chromium	Cr	7440-47-3		0.002 mg/L	
Cadmium	Cd	7440-43-9		0.001 mg/L	
Nickel	Ni	7440-02-0		0.002 mg/L	
Lead	Pb	7439-92-1		0.003 mg/L	
Zinc	Zn	7440-66-6		0.001 mg/L	
Phthalates					
Dimethyl phthalate	DMP	131-11-3	LLE-GC/MS(SIM)	0.4 / 0.3 µg/L*	UG
Diethyl phthalate	DEP	84-66-2	(BSTFA	0.3 / 0.2 µg/L*	
Diisobutyl phthalate	DIBP	84-74-2	derivatization)	0.3 / 0.2 µg/L*	
Dibutyl phthalate	DBP	84-74-2		0.3 / 0.2 µg/L*	
Bis(2-ethylhexyl) phthalate	DEHP	117-81-7		0.1 / 0.1 µg/L*	
Di-n-octyl phthalate	DNOP	117-84-0		0.1 / 0.1 µg/L*	

Analytes	Acronym	CAS	Analytical method	MDL (water samples)	Analysis laboratory
Alkylphenols (APs)					
4-t-octylphenol	4-T-OP	140-66-9	SPE-GC/MS(SIM)	4 / 2 ng/L*	UG
4-octylphenol	4-OP	1806-26-4	(BSTFA	5 / 2 ng/L*	
4-nonylphenol	4-NP	104-40-5	derivatization)	3 / 2 ng/L*	
4-tert-octylphenol monoethoxylate	4-T-OP-MET	2315-67-5		5 / 2 ng/L*	
4-tert-octylphenol diethoxylate	4-T-OP-DET	2315-61-9		4 / 2 ng/L*	
Nonylphenol diethoxylate	NP-DET	EC Number 200-662-2 (Sigma Aldrich)		3 / 1 ng/L*	
Nonylphenol monoethoxylate	NP-MET	EC Number 200-662-2 (Sigma Aldrich)		5 / 1 ng/L*	
Bisphenols					
Bisphenol A	BPA	1980-05-07	SPE-GC/MS(SIM) (BSTFA derivatization)	3 / 1 ng/L*	UG
Perfluoroalkyl Substances (PFAS)					
perfluoroalkyl carboxylates (PFCAs)					
Perfluorobutanoate	PFBA	375-22-4	SPE- LC-MS/MS	6.8 ng/L	SLU
Perfluorohexanoate	PFHxA	307-24-4		0.08 ng/L	
Perfluoroheptanoate	PFHpA	375-85-9		0.08 ng/L	
Perfluorooctanoate	PFOA	335-67-1		0.08 ng/L	
Perfluoroalkane sulfonates (PFSAs)					
Perfluorobutane sulfonate	PFBS	375-73-5 or 59933-66-3	SPE- LC-MS/MS	0.41 ng/L	SLU
Perfluorohexane sulfonate	PFHxS	355-46-4		0.08 ng/L	
Perfluorooctane sulfonate	PFOS	1763-23-1		0.08 ng/L	
Perfluorodecane sulfonate	PFDS	335-77-3		0.08 ng/L	
Pharmaceuticals					
Diclofenac	DIC	15307-86-5	SPE-GC/MS(SIM)	6 / 3 ng/L*	UG
17 α -ethinylestradiol	EE2	57-63-6	(BSTFA	7 / 2 ng/L*	
17 β -estradiol	E2	50-28-2	derivatization)	5 / 2 ng/L*	

* A / B – MDL respectively for wastewater / stormwater

3 RESULTS AND DISCUSSION OF HAZARDOUS SUBSTANCE SCREENING IN MUNICIPALITIES

The results of the chemical analysis of wastewater and sludge samples were used to calculate detection frequencies and map the distribution of hazardous substances in pilot municipalities. The concentrations of analytes are presented with different units, depending on the hazardous substance and sample type. In the following sections the results are summarized as detection frequencies, median and minimum/maximum measured concentrations. For the calculation of median values, half of the detection limit concentration (MDL) was used if the analyte was not detected. In the following sections for each target hazardous substance the results of the chemical analyses are presented together with additional information on e.g. uses and sources, policy relevance and conclusions drawn from the frequency of detection and distribution in wastewater types.

The results of the chemical analyses are presented in tables showing descriptive statistic values of measured concentrations and detection frequencies. The different ranges of detection frequencies are indicated as follows.



The acronyms assigned to the wastewater sample types are presented in Table 2 (Chapter 2).

3.1 Metals

Unlike to man-made organic hazardous substances, metals are naturally occurring substances. Some metals are essential trace elements which are important for the well-being of organisms when present in the proper amount. However, in larger amounts metals can cause acute and chronic toxicity.

For the analysis of the different samples from the sewage system and WWTP the following trace metals were chosen as targets: chromium (Cr), copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd) and lead (Pb). These metals are usually the most common toxic elements analysed and found in wastewater.

Cadmium and lead are trace metals with no essential function in living organisms. They may cause toxic effects when physiological mechanisms like excretion, storage and detoxification are no longer able to prevent excessive body levels.

Because trace metals accumulate in aquatic sediments and the food chain, they have been an important part of water quality monitoring programmes for many years. Different legal acts of the EU pursue the goal of protecting humans and biota from excessive exposure to toxic metals, either by setting maximum levels of certain metals in foodstuffs and feed or by setting quality standards for products and articles or environmental matrices. The WFD regulates levels of cadmium, lead and nickel and their compounds which are listed as priority substances with EQS for surface waters. Cadmium and lead are also included in the HELCOM set of core indicators for hazardous substances and their effects. Cadmium and lead compounds are included in the REACH candidate list because of their particular toxic properties. Since 2015, chromium compounds have been included in the REACH restricted substance list (Annex XVII) with a requirement that it shall not occur in leather articles coming in contact with the skin in concentrations equal to or greater than 3 mg/kg of the total dry weight of the leather.

The results of the chemical analysis of metals are summarized in **Table 4**.

Chromium was detected in only three samples of wastewater; one from a residential area and two from areas where small-medium enterprises are present. The chromium concentrations were low, the maximum value not higher than 0.009 mg/L. Lead was detected in all kinds of wastewater samples except those from WWTPs. The detection frequencies were rather low and the concentrations in the range from 0.007 to 0.031 mg/L. Cadmium was detected more often than chromium and lead. In wastewater samples from the sewage system, from stormwater and WWTP the detection frequencies ranged from 33% to 89% with highest values observed in samples from small and medium enterprises and WWTP effluent. The range of concentrations measured in each water sample type were similar with the highest values ranging from 0.008 to 0.012 mg/L. Nickel showed overall detection frequencies of 72% and 67% in wastewater from residential areas and in stormwater respectively. Higher detection frequencies (78 – 86%) were observed in wastewater from industrial areas, small and medium enterprises and WWTPs. Copper and zinc were detected in all analysed samples regardless of sampling location type. Copper and zinc concentrations varied from 0.001 to 0.349 mg/L and 0.003-3.089 mg/L respectively.

As one can see from the results of the analysis of WWTP sludge samples, metals have a high tendency to absorb to particulate matter leading to an accumulation in sludge. Compared to concentration levels in the water phase sludge always had higher metal concentrations.

Table 4: Summary of results of the screening of target metals in wastewater sample types. Wastewater from residential area (RA), stormwater (SW), sewage water from industrial areas (IA), small and medium-sized enterprises effluents (SME), influent sewage water (ISW), effluent sewage water (ESW), sewage sludge (SS)

Metals	General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
Chromium (Cr)								
detected/analysed	3/92	1/19	0/12	2/20	0/18	0/14	0/9	5/5
% of detection	3	5	0	10	0	0	0	100
Min - Max (mg/L; SS:mg/kg dm)	0-0.009	0.009	0	0.006-0.009	0	0	0	24-47
Median	0.001	0.001	0	0.002	0	0	0	36
Copper (Cu)								
detected/analysed	92/92	19/19	12/12	20/20	18/18	14/14	9/9	5/5
% of detection	100	100	100	100	100	100	100	100
Min - Max (mg/L; SS:mg/kg dm)	0.001-0.349	0.001-0.068	0.007-0.076	0.002-0.349	0.001-0.055	0.007-0.113	0.001-0.065	96-270
Median	0.042	0.034	0.036	0.079	0.016	0.051	0.02	199
Zinc (Zn)								
detected/analysed	92/92	19/19	12/12	20/20	18/18	14/14	9/9	5/5
% of detection	100	100	100	100	100	100	100	100
Min - Max (mg/L; SS:mg/kg dm)	0.003-3.089	0.068-0.370	0.004-0.499	0.007-3.089	0.003-0.763	0.015-0.356	0.014-0.115	625-978
Median	0.200	0.164	0.148	0.418	0.129	0.177	0.039	834
Nickel (Ni)								
detected/analysed	72/92	14/19	10/12	17/20	12/18	12/14	7/9	5/5
% of detection	78	72	83	85	67	86	78	100
Min - Max (mg/L; SS:mg/kg dm)	0.003-0.039	0.003-0.037	0.007-0.039	0.003-0.039	0.003-0.033	0.003-0.036	0.008-0.011	18-31
Median	0.011	0.009	0.015	0.011	0.009	0.015	0.007	23
Cadmium (Cd)								
detected/analysed	61/92	11/19	4/12	17/20	12/18	9/14	8/9	5/5
% of detection	67	56	33	86	67	64	89	100
Min - Max (mg/L; SS:mg/kg dm)	0.001-0.012	0.002-0.009	0.002-0.008	0.001-0.010	0.002-0.010	0.002-0.010	0.002-0.012	4-8
Median	0.003	0.002	0.002	0.004	0.004	0.004	0.003	6
Lead (Pb)								
detected/analysed	8/92	1/19	1/12	1/20	4/18	0/14	0/9	5/5
% of detection	9	5	8	10	22	0	0	100
Min - Max (mg/L; SS:mg/kg dm)	0-0.031	0.012	0.031	0.01-0.025	0.007-0.015	0	0	3-33
Median	0.003	0.002	0.004	0.003	0.003	0	0	19

Figure 1 below presents the detection frequencies of target metals in participating municipalities and the overall detection frequencies in analysed wastewater samples. All metals were observed in samples from all municipalities with copper and zinc detected in all samples and nickel and cadmium detected in about 80% and 70% respectively. Lead was detected in samples from five and chromium in samples from four municipalities. The detection frequencies of both metals were low.

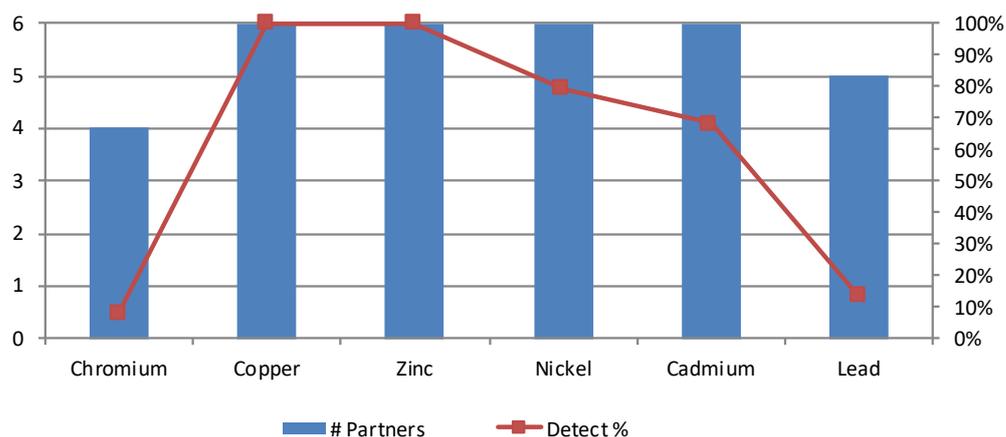


Figure 1: Number of municipalities where metals were found in sewage water (# Partners) and the overall detection frequency (Detect %).

Trace metals are ubiquitous in the environment and a significant part of natural and anthropogenic emissions released to wastewater are transferred further to WWTPs. Results of the screening suggests that major urban inputs of trace metals to wastewater include household effluents and emissions from small enterprises (e.g. car washes). Toxic trace metals may be present in food, consumer products, articles and materials. Relevant sources of metals in domestic wastewater are cosmetic products and faeces. Atmospherically deposited metals and emissions related to traffic, buildings and construction can be transported with stormwater into the sewage system.

A study on metal loads in stormwater runoff from traffic road-deposited sediments showed that cadmium had the highest loads in the stormwater wash-offs, which is in line with a high leaching rate from sediments for this substance. The trace metals, which were analysed in unfiltered samples, accumulated primarily to the fine sediment fraction (<250 µm) (Zara et al., 2017).

The concentrations of toxic trace metals such as cadmium, lead, chromium and some others have been measured for a long time in Baltic Sea environment. Natural background concentrations are usually very low. However, emissions from anthropogenic activities have caused markedly higher metals levels in certain areas. Trace metals accumulate easily in the fine fraction of sediments, from where they may be taken up by bottom-dwelling biota. For that reason blue mussels have been used as an indicator of metal pollution for many years (HELCOM, 2010).

3.2 Phthalates

Phthalates are a group of chemicals based on the same chemical structure and produced in large volumes. Most phthalates are added to plastic to improve its softness, flexibility and resilience. For example, in polyvinylchloride (PVC), phthalates may constitute up to 50% by weight of plastic. For a long time diethylhexyl phthalate (DEHP) was the most commonly produced phthalate. It has been partly replaced by diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) which together are now most commonly used. DEHP is possibly one of the most widespread organic hazardous substances. Because phthalates are semi-volatile organic compounds they are continuously released during the whole life cycle of goods and products. Phthalates are used in a multitude of products and articles of daily life, for example in cosmetics, personal care and household products, food packaging, toys, electronics, building materials and medical devices.

Because of their widespread presence in articles and materials phthalates are ubiquitous contaminants in the indoor environment. Humans are exposed to phthalates when, for examples, they touch products containing phthalates. Food packaging may contain phthalates, which may migrate to fatty food like meat and dairy products. Furthermore, phthalates adsorb to dust particles and can be inhaled. As a component of floor-cleaning water phthalates may be transferred to the sewage system. Phthalates emitted to the air may be deposited to urban surfaces and washed off to stormwater sewers.

Phthalates are of generally low acute toxicity. However, some of them are documented EDCs and are suspected to affect reproductive and developmental functions in humans and animals. Of particular

concern are potential adverse impacts on male reproductive development. Observed effects in rodent studies led to the assumption that phthalates are one of the factors responsible for declining fertility, testicular cancer and falling sperm counts in European men (Knez, 2013).

For the analytical screening of urban wastewater samples the following phthalates were chosen: dimethyl phthalate (DMP); diethyl phthalate (DEP); diisobutyl phthalate (DIBP); dibutyl phthalate (DBP); diethylhexyl phthalate (DEPH) and di-n-octyl phthalate (DNOP). These six phthalates have also been chosen by the US Environmental Protection Agency (EPA) for monitoring in water and sediment. Five of them are also included in the EPA priority pollutant list. Overall the selected substances comprise a wide range of physical and chemical properties and therefore could be considered as typical and representative for the whole class of compounds in terms of their occurrence, environmental fate and potential toxicity.

Concerning **EU restrictions**, six phthalates are currently included in REACH Annex XVII as substances with restricted use in toys and childcare articles. The concentrations of DEHP, DBP, and BBP (Benzyl butyl phthalate) must be below 0.1% by weight in PVC and plasticized materials in all toys and childcare articles. The same requirements apply to DINP, DIDP and DNOP in toys which can be placed in the mouth. DEHP, DIBP and DNBP are also included in the REACH list of SVHC for hazardous substances be subjected for authorization. DEHP is included in the WFD list as priority hazardous substance and the environmental quality standard within the frame of the WFD has been set. The EU regulation 10/2011 on plastic materials and articles intended to come into contact with food concern phthalates as well.

The results of the analyses of selected phthalates in samples of wastewater and from WWTPs are summarized in **Table 5**.

In general, the detection frequencies of phthalates were high to very high. Phthalates were present in all water samples, with the exception of stormwater samples (82%). There was no clear correlation between the detection frequency and the size of each municipality. The highest concentrations of total phthalates were detected in water samples from industrial areas (mean value almost 1200 µg/L), but they varied in a broad range from 8 to more than 10000 µg/L. This is consistent with a frequent use of phthalates in many different materials and processes. Relatively high concentrations were also observed in WWTP wastewaters (mean values were 260 µg/L in influents and 849 µg/L in effluents). It is of special interest that, at least in certain moments, the mean concentration was higher in effluents, which may suggest some phthalate release from wastewater treatment plants. Moreover, it also suggests that the currently applied treatment technologies are insufficient to remove those compounds from the wastewater. The lowest phthalate concentrations were determined in wastewater samples from residential areas (177 µg/L) and in stormwater samples (29 µg/L). Very high phthalate concentrations were also observed in sludge samples (81-299 mg/kg dry weight), which is justified by the hydrophobic nature of these compounds.

The detection frequencies of single phthalates varied, depending on their physiochemical properties. The most hydrophilic DMP was rarely detected in water samples (17%) and was absent in all sludge samples. In contrast, the most hydrophobic di-n-octyl phthalate (DNOP) was present in all sludge samples as expected, and its detection frequency in water samples was only moderate (32%). These two compounds were also present at the lowest concentrations in water samples, with mean values not exceeding 6 µg/L. The most abundant compound in water samples of all types was dibutyl phthalate (DBP) (mean value 1128 µg/L in wastewater samples from industrial areas and 151-754 µg/L in WWTP influent and effluent samples). It must be, however, noted, that the highest concentrations, which were detected in single samples greatly exceeded mean values. The second major compound in water samples was diethylhexyl phthalate (DEHP), which was particularly abundant in WWTP influent and effluent samples. It was also the most abundant phthalate in sludge samples (128 mg/kg dry weight), followed by dibutyl phthalate (DBP) (41 mg/kg dry weight). This is somehow consistent with both their wide use in industrial processes and their hydrophobic nature.

Table 5: Summary of results of the screening of target phthalates in wastewater sample types. Wastewater from residential area (RA), stormwater (SW), sewage water from industrial areas (IA), small and medium-sized enterprises effluents (SME), influent sewage water (ISW), effluent sewage water (ESW), sewage sludge (SS)

Phthalates		General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
dimethyl phthalate (DMP)									
detected/analysed		15/87	5/18	1/12	3/18	1/17	5/14	0/8	0/5
% of detection		17	28	8	17	6	36	0	0
Min - Max	(mg/L; SS:mg/ kg dm)	1.5-7.6	1.7-3.3	4.7	1.8-3.4	7.6	1.5-3.5	0	0
Median		0.6	0.7	0.6	0.6	0.6	0.8	0.2	0.1
diethyl phthalate (DEP)									
detected/analysed		72/87	18/18	11/12	14/18	8/17	13/14	8/8	5/5
% of detection		83	100	92	78	47	93	100	100
Min - Max	(mg/L; SS:mg/ kg dm)	0.7-194.8	3.0-78.5	1.4-90.1	2.2-194.8	0.7-2.3	1.39-81.86	1.0-12.1	1.1-3.3
Median		22.7	25.6	16.21	45.60	0.7	30.9	6.1	1.7
diisobutyl phthalate (DIBP)									
detected/analysed		71/87	16/18	11/12	16/18	6/17	14/14	8/8	5/5
% of detection		82	89	92	89	35	100	100	100
Min - Max	(mg/L; SS:mg/ kg dm)	1.30-277.4	2.1-29.4	1.60-103.3	2.0-277.4	1.3-14.4	4.1-65.5	5.2-133.1	9.2-37.0
Median		19.2	7.8	17.0	36.3	1.6	22.4	43.1	16.5
dibutyl phthalate (DBP)									
detected/analysed		74/87	16/18	12/12	17/18	7/17	14/14	8/8	5/5
% of detection		85	89	100	94	41	100	100	100
Min - Max	(mg/L; SS:mg/ kg dm)	0.6-9913.4	0.6-555.4	1.5-9913.4	1.3-1691.7	1.0-216.7	1.4-847.5	3.4-2805.8	15.4-109.6
Median		312.5	130.1	1128.2	166.8	24.1	151.0	754.2	40.7
diethylhexyl phthalate (DEHP)									
detected/analysed		80/87	18/18	12/12	17/18	11/17	14/14	8/8	5/5
% of detection		92	100	100	94	65	100	100	100
Min - Max	(mg/L; SS:mg/ kg dm)	0.4-555.0	0.9-52.1	0.4-186.3	1.9-294.4	0.4-4.0	4.8-555.0	1.5-378.2	38.5-204.5
Median		30.1	11.5	25.2	51.8	1.4	53.0	53.3	128.0
di-n-octyl phthalate (DNOP)									
detected/analysed		28/87	8/18	4/12	5/18	2/17	6/14	3/8	5/5
% of detection		32	44	33	28	12	43	38	100
Min - Max	(mg/L; SS:mg/ kg dm)	1.1-69.8	1.9-7.0	2.4-3.7	1.3-69.8	1.1-2.0	1.7-5.4	1.5-4.2	8.3-44.1
Median		2.0	1.5	1.1	5.9	0.2	1.4	1.1	24.0

In **Figure 2** the presence of target phthalates in municipalities and the overall detection frequencies are presented. The detection frequencies of most phthalates were quite similar, ranging from 80-90% in all municipalities. DMP showed the lowest and DNOP a moderate detection frequency. Compared to these two compounds all the other phthalates were considerably more abundant. Each phthalate substance was detected in wastewater samples from all tested municipalities.

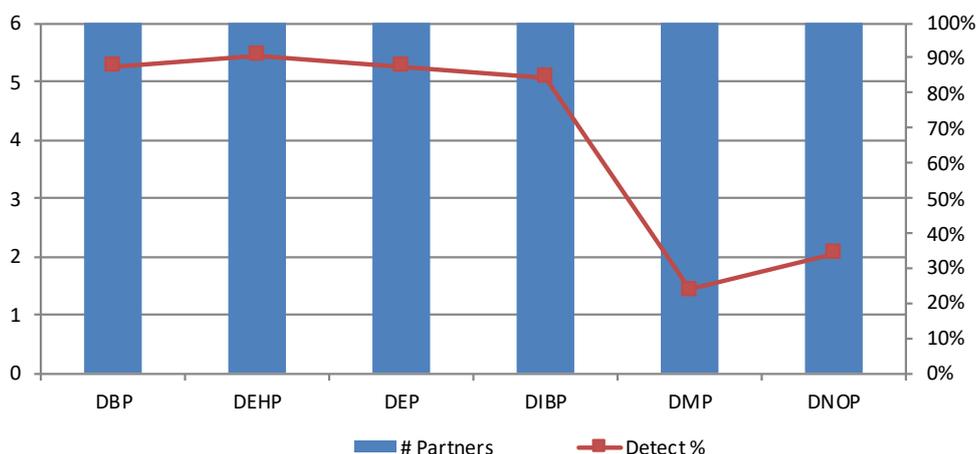


Figure 2: Number of municipalities where phthalates were found in sewage water (# Partners) and the overall detection frequency (Detect %). (DBP - dibutyl phthalate, DEHP - diethylhexyl phthalate, DEP - diethyl phthalate, DIBP - diisobutyl phthalate, DMP - dimethyl phthalate, DNOP - di-n-octyl phthalate)

The frequent detection of phthalates in wastewater samples from different urban areas and in stormwater and from WWTP reflects the ubiquitous occurrence of this class of substance in all kinds of environmental matrices (Ahrens & Bundschuh, 2014).

Concerning households, it is well known that phthalates, like other hazardous substances, are emitted to municipal wastewater. The emissions are derived from everyday activities such as cleaning and laundry. In a Swedish study five of ten analysed phthalates were observed in graywater from a residential area. DEHP showed the highest mean concentration (15.2 µg/L) which is in the range observed in the current study. Other phthalates were present in lower concentrations (Almqvist et al., 2006).

Phthalates adsorbed to household dust may be transferred to graywater via floor-cleaning water. Phthalates are a common component of dust as has been shown in a study performed with dust samples from apartment buildings in Stockholm. Eight phthalates were detected in almost all samples, with DEHP being the most abundant compound (Luongo & Östman, 2016). Another Swedish study revealed the abundant presence phthalates in dust samples from preschools (Larsson et al., 2017). Within the NonHazCity project phthalates have been analysed in dust samples from ten private residences in Stockholm. The eight analysed phthalates were detected in all samples, with DEHP and DINP being the most abundant compound (Giovanoulis, 2017).

Stormwater from urban areas is another pathway whereby phthalates are transferred to the sewage system or directly to surface waters. For instance, in a Swedish study the presence of eight phthalates were analysed in urban stormwater samples from three catchment areas, two urban residential areas and one high-density traffic area. All of the eight phthalates were measured above detection limits although with different detection frequencies. The low molecular weight DMP occurred in lower concentrations in stormwater than the higher molecular weight DEHP (Björklund et al., 2009).

The current findings on concentrations of phthalates in samples from WWTP fall into line to with published previous findings. For example, in a study the fate of six phthalates in 15 WWTPs were investigated. All six phthalates detected in influent water were observed in effluent water as well, but in notably lower concentrations. DEHP (3.4 – 34 µg/L) was the most abundant compound in influent water, followed by DEP (0.77 – 9.2 µg/L) and DBP (n.d. – 8.7 µg/L). Also in the effluent DEHP and DBP were the most abundant compounds. Removal of phthalates is due to biotransformation and adsorption to solid particles (sludge). The removal via adsorption to sludge increased with increasing molecular weight and increasing lipophilic character of the compound (Clara et al., 2010).

Sewage sludge may contain relatively high concentrations of phthalates, with DEHP being the predominant component adsorbing on sludge solids because of its hydrophobicity. Thus, the use of sewage sludge as a soil amendment is a potential route of phthalate esters to the terrestrial environment.

In relation to the **Baltic Sea** there are very few data available on concentrations of phthalates in environmental matrices such as sediment and biota. Representative phthalate proxies are not included in continuous biota monitoring programs, thus the phthalate burden of Baltic Sea biota is unknown. One may expect that this may change in the future, since, within the frame of WFD monitoring, concentrations of the priority pollutant DEHP have to be measured at least in surface water.

Since some phthalates have similar modes of action one may conclude that the overall health or environmental risk increases when exposed to the current widespread mixture of different phthalates.

In chapter 5 of this report a source map for phthalates is presented, which was elaborated for some of the partner municipalities of the NonHazCity project.

3.3 Alkylphenols

Alkylphenols (APs) and alkylphenol ethoxylates (APEO) are a group of hazardous substances with similar chemical structure and non-ionic surfactant properties. Within the group of alkylphenols nonylphenols (NP) and their ethoxylates (NPE) and octylphenols (OP) and their ethoxylates (OPE) were chosen as targets. The majority of produced alkylphenols are in fact NPEs.

NPEs are mainly used as cleaning agents and detergents in various applications. NP/NPEs are also added to plastics and rubbers, pesticides, pharmaceuticals, cosmetics paints and coatings, agro-chemicals and chemicals used in paper making. Furthermore, NP/NPEs are used for the treatment of textiles. NPEs degrade rather easily to short-chained NPEs and NP which are toxic to aquatic organisms. Since NP/NPEs are lipophilic, they adsorb to sewage sludge in WWTPs and accumulate in sediments and biota. NPEs can enter the body by inhalation of air containing NPEs, ingestion of contaminated food or water, or by dermal contact with products containing NPEs.

OP (4-tert-octylphenol) is used for the production of phenolic resins and as a plasticizer and antioxidant in plastics and resins. OPEs are present in cleaning products such as detergents, industrial cleaners, and emulsifiers, but also in lesser quantities in many other applications, such as pesticides, pulp and paper production, textiles, water-based paints and varnishes.

In general, both NP/NPE and OP/OPE are classified as very toxic to aquatic organisms. Of special concern are their experimentally verified EDC properties. Because of their chemical structure this class of substances is able to bind to important hormone receptors in vertebrates. In humans they are suspected of impairing fertility and causing harm to unborn children. Fish exposure to NP and OP may cause reproductive disorders like malformation of gonads or feminization of male fish.

The chosen target alkylphenols are of relevance for several policy settings. Both NP and NPE are on the REACH annex XVII restricted substances list and their use in EU is almost eliminated. They shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0.1 % by weight for several purposes.

Furthermore, 4-nonylphenol (branched and linear, ethoxylated) and 4-tert-octylphenol have been added to REACH Annex XIV (SVHC). Their use must be phased out in the EU by January 2021. 4-nonylphenol and 4-octylphenol (including isomer 4-tert-octylphenol) are included in the WFD list of priority substances. For both hazardous substances EQS within the frame of the WFD have been set. HELCOM has selected NP/NPE and OP/OPE as hazardous substances of specific concern to the Baltic Sea.

The analytical screening in pilot municipalities showed that alkylphenols were present in all types of wastewater samples (**Table 6**). The concentrations of 4-NP ranged from 10 to 281 ng/L in stormwater and wastewater. There are, several factors that may explain such low concentrations of 4-NP in wastewater observed in this study. The most important is the fact that 4-NP is subject to biological degradation. Detection frequencies of 4-NP are low to high. Higher concentrations in the range from 29-774 ng/L and 17-5506 ng/L were noted for 4-OP and 4 t-OP, respectively. The highest concentration of these compounds was determined in wastewater from residential area and in samples of WWTP wastewater. Thus one can suggest, that residential areas are main sources of 4-OP and 4-t-OP in WWTPs. General detection frequencies of 4-OP were low, however detection frequencies of this compound were moderate to high in WWTPs. Nonylphenol monoethoxylate (NP-MET) was present in the tested samples at similar levels of concentrations as 4-t-OP and its concentration ranged from 214-6613 ng/L. The highest concentration of these compounds was determined in wastewater from residential areas and in influent and effluent water from WWTPs. The highest frequency of detection was observed in influent and effluent WWTP samples (WWTP influents: 42%; WWTP effluents: 50%) and in sewage sludge samples (SS: 33%). For other types of samples detection frequency was significantly lower (0-18%). Much lower concentrations of 4-tert-octylphenol diethoxylate (4-t-OP-DET) and nonylphenol diethoxylate (NP-DET) were noted. The concentration of these compounds is within the range of 38-299 ng/L and 103-244 ng/L, respectively. Moreover, the frequency of detection of these compounds was low (<12% in water samples). However, for 4-t-OP-DET the higher detection frequency was found for WWTP influent and effluent samples (25%).

Table 6. Summary of results of the screening of target alkylphenols in wastewater sample types. Wastewater from residential area (RA), stormwater (SW), sewage water from industrial areas (IA), small and medium-sized enterprises effluents (SME), influent sewage water (ISW), effluent sewage water (ESW), sewage sludge (SS)

Alkylphenols		General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
4-tert-Octylphenol (4-t-OP)									
detected/analysed		30/84	5/17	2/12	8/17	3/18	7/12	5/8	1/3
% of detection		36	29	17	47	17	58	62	33
Min - Max	(mg/L; SS:mg/ kg dm)	17-5506	71-4904	451-688	162-972	83-2285	53-2517	17-5506	0.44
Median		386	586	97	208	190	383	855	0.18
4-Octylphenol (4-OP)									
detected/analysed		19/84	3/17	0	2/17	1/18	8/12	5/8	1/3
% of detection		23	18	0	12	6	67	62	33
Min - Max	(mg/L; SS:mg/ kg dm)	29-774	42-357	0	56-137	54	39-774	29-105	0.88
Median		47	26	0	12	4	158	36	0.33
4-Nonylphenol (4-NP)									
detected/analysed		22/84	6/17	0	5/17	1/18	9/12	1/8	1/3
% of detection		26	35	0	29	6	75	12	33
Min - Max	(mg/L; SS:mg/ kg dm)	10-281	33-281	0	28-137	47	10-190	39	0.14
Median		25	36	0	16	4	65	6	0.06
4-tert44-tert-Octylphenol monoethoxylate (4-t-OP-MET)									
detected/analysed		14/84	3/17	1/12	1/17	0/18	6/12	3/8	1/3
% of detection		17	18	8	6	0	50	38	33
Min - Max	(mg/L; SS:mg/ kg dm)	12-514	12-514	95	489	0	44-167	36-106	0.28
Median		26	35	10	27	0	58	27	0.12
n-NNonylphenol monoethoxylate (NP-MET *)									
detected/analysed		13/84	1/17	0	3/17	0/18	5/12	4/8	1/3
% of detection		15	6	0	18	0	42	50	33
Min - Max	(mg/L; SS:mg/ kg dm)	214-6613	1029	0	520-732	0	214-4973	1084-6613	3.22
Median		517	56	0	92	0	1029	1408	1.11
4-tert-Octylphenol diethoxylate (4-t-OP-DET)									
detected/analysed		6/84	0/17	0	0	1/18	3/12	2/8	0
% of detection		7	0	0	0	6	25	25	0
Min - Max	(mg/L; SS:mg/ kg dm)	38-299	0	0	0	277	38-299	64-169	0
Median		16	0	0	0	13	36	30	0
Nonylphenol diethoxylate (NP-DET)									
detected/analysed		3/84	1/17	0	0	0	1/12	1/8	0
% of detection		4	6	0	0	0	8	12	0
Min - Max	(mg/L; SS:mg/ kg dm)	103-244	103	0	0	0	244	200	0
Median		12	8	0	0	0	23	27	0

4-nonylphenol, 4-octylphenol and 4-tert-octylphenol were detected in samples from all six municipalities, whereas the detection frequency of the other alkylphenol compounds were in the range of two to five municipalities. With regard to all analysed samples the detection frequencies were at most

about 30% and otherwise lower. 4-tert-octylphenol was generally detected most often, whereas the two diethoxylate compounds had the lowest detection frequencies (Figure 3).

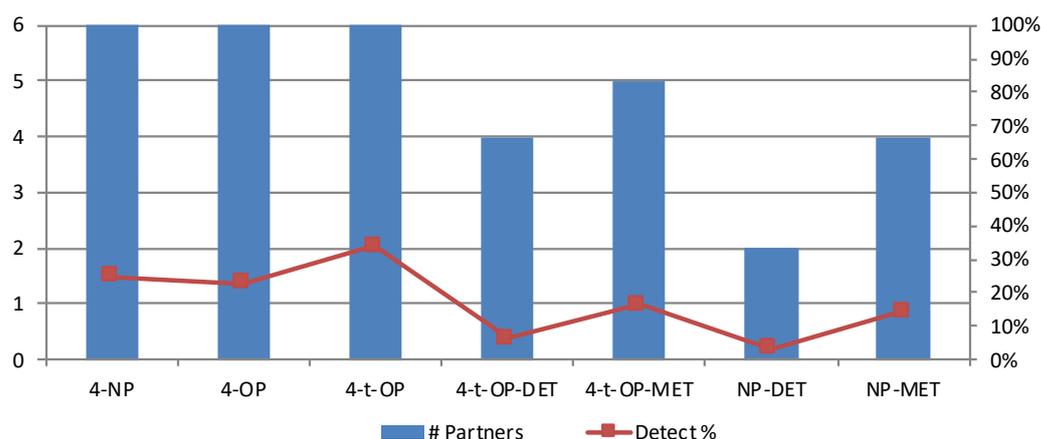


Figure 3: Number of municipalities where alkylphenols were found in sewage water (# Partners) and the overall detection frequency (Detect %). (4-NP - 4-Nonylphenol, 4-OP - 4-Octylphenol, 4-t-OP - 4-tert-Octylphenol, 4-p-OP-DET - 4-tert-Octylphenol diethoxylate, 4-t-OP-MET - 4-tert-Octylphenol monoethoxylate, NP-DET - Nonylphenol diethoxylate, NP-MET - Nonylphenol monoethoxylate)

Although the general detection frequencies of alkylphenols were considerably lower than for e.g. phthalates, representatives of this substance group have been observed in all types of wastewater samples.

As part of the Swedish study mentioned above concerning phthalates, several compounds of NPEs have been detected in graywater from apartments in a residential area. During the sampling period, rather large variations of concentrations were noted, with levels sometimes below detection limits (Almqvist et al. 2006). In principle this finding is in line with the current pilot screening, where the detection frequency of alkylphenols was rather low when compared to other target hazardous substances analysed. Nevertheless the current findings show that NP and OP and their ethoxylates are still widely present in urban wastewater despite all regulations to reduce their occurrence in products and articles.

Imported textiles which are still produced using alkylphenols in several process steps e.g. dyeing and bleaching are regarded as one major emission pathway for NP/NPEs (Rasmussen et al., 2013). In 2015 extended restrictions on imports of clothing and other textile products containing NPE were adopted by the European Commission, suggesting this is no longer such an important source as it once was.

Considering stormwater, the same as what has been noted for phthalates applies for NP and NPEs. Thus nonylphenol mono- and di-ethoxylate have been observed in a stormwater sedimentation facility and in stormwater itself. Overall branched NP and lower NPEs have been detected in Swedish urban water systems. Stormwater from traffic or industrialized areas (e.g. car washes) may contain higher alkylphenol loads (Björklund et al., 2009). Alkylphenols and their ethoxylates have been identified as one significant group of pollutants in the urban road and traffic environment (Markiewicz et al., 2017).

As expected, the detection frequencies of alkylphenols in samples taken from WWTPs were higher than in samples from points upstream the sewage system or in stormwater samples. Household activities are recognized as substantial contributors to the discharges of nonyl- and octylphenoles and their ethoxylates to WWTPs.

In a review of the occurrence and fate of hazardous substances in WWTPs the range of published concentrations for NP in influent water is reported as <0.03-101.6 µg/L and for effluent water <0.03-7.8 µg/L, which correspond to removal rates of 21.7-99% (Luo et al., 2014). For octylphenol, influent and effluent concentrations were <0.2-8.7µg/l and 0.0004-1.3 µg/L respectively (removal rate <0-96.7%). Overall NP is one of the most frequently detected hazardous substance in WWTP. The removal rate of alkylphenols is dependent on WWTP-specific wastewater treatment conditions and processes (Luo et al., 2014). Since alkylphenols have a tendency to adsorb to suspended solids sludge is an important sink for these substances in WWTPs.

In a HELCOM report on eight organic hazardous substances of specific concern to the Baltic Sea NP/NPEs and OP/OPEs are considered (HELCOM, 2009). HELCOM concluded that the few available monitoring

data indicate that NP and OP levels in sea water and fish are not high, but sediment levels may cause adverse chronic effects for benthic organisms. WWTPs effluents are considered as relevant discharges of alkylphenols to the Baltic Sea which may cause adverse effects on biota.

Polish field studies performed in the Gulf of Gdańsk have demonstrated the presence of 4-t-OP and 4-NP in zooplankton (Staniszewska et al., 2016) and the accumulation of these substances in the soft-body of blue mussel (Staniszewska et al., 2017). In fish, the endocrine disruptor NP induced the synthesis of the female egg precursor protein vitellogenin in male eelpout, a viviparous fish prevalent in the Baltic Sea (Christiansen et al., 1998). Exposure of pregnant female eelpout to 4-t-OP led to accumulation of this substance in plasma and ovarian fluid and caused marked effects on the developing embryos (Rasmussen et al., 2002).

3.4 Bisphenol A

Bisphenol A (BPA) is one of the highest production volume hazardous substance in the world. Most of the BPA produced is used to make polycarbonate plastics and to a lesser extent epoxy resins. BPA production has grown steadily due to the increasing demand for plastic. Polycarbonate plastics are often used in plastic food-storage containers, reusable water bottles. Epoxy resins are used to coat the inside of food, beverage cans, and water-supply pipes. BPA is also found in many daily-use products and articles including digital media (e.g., CDs and DVDs), electronic equipment, thermal paper products (e.g., cash register receipts), kitchen tools, toys, and medical devices. Furthermore, flooring, furniture and building material can contain BPA. Hence, releases to indoor and outdoor environments probably occur from a wide range of common products and materials.

BPA is an EDC. Due to the ubiquitous exposition of humans in industrialized countries to low BPA doses BPA is found in almost all urine and blood samples tested (Michalowicz, 2014).

The adverse health effects linked with BPA include: cancer (breast, prostate), altered immune system function and effects on reproduction. However, the effects of BPA on humans are still not well understood, and the issue is controversial. In laboratory studies and surveys of wildlife, several harmful effects from reproductive impairment to neurobehavioral conditions and cancer have been identified. There is still an ongoing debate, whether BPA current exposure levels are sufficiently high that humans may suffer adverse health effects.

Because of its hazardous properties BPA is subject to restrictions in the EU. BPA was added to the REACH candidate list of SVHC because of its effects on reproduction (classification reprotoxic 1B). From January 2020 the share of BPA in thermal paper (cash register receipts) has to be reduced to less than 0.02% BPA by weight. Since 2011 BPA has been banned in baby feeding bottles under the European Commission Directive 2011/8/EU. BPA is also banned in the manufacture of packaging of goods for infants and young children (0-3 years). For food contact plastics, Regulation (EU) No 10/2011 includes a draft amendment which establishes a new specific migration limit of 0.05 mg/kg food for BPA in varnishes or coatings applied to materials or articles intended for food contact.

The current snap-shot screening revealed a very high detection frequency of BPA in all types of wastewater samples (**Table 7**). Highest average concentrations were observed in the samples collected close to SME and/or industrial areas (2620 ng/L and 1883 ng/L, for SME and industrial area samples, respectively, which is consistent with use patterns. The results of chemical screening demonstrate that significant sources of BPA are present upstream of WWTPs.

Much lower concentrations of BPA were observed in samples collected from residential areas and in stormwater samples. However, the high detection frequency suggests that BPA containing products are commonly used in private households, and that the use of such products or materials contributes to the presence of BPA in wastewater.

BPA was present in wastewater samples from all six municipalities. The detection frequency ranged from 50% to almost 100%. In WWTPs the removal rates for BPA are generally higher compared to the other organic target hazardous substances. This is consistent with the results of the current screening which showed a lower detection frequency and mean concentrations in effluent water compared to influent water. In a classification of hazardous substances based on removal efficiency in conventional wastewater treatment processes BPA was listed in the “highly removed” (>70%) group (Luo et al., 2014). The high removal rate is mainly due to biodegradation and absorption to solid sludge particles. In WWTP samples, the concentrations in the influents (medium value 775 ng/L and the highest detected BPA concentration 2962 ng/L) were generally higher than the effluents (median value 112 ng/L and the

highest detected BPA concentration 481 ng/L). This suggests that even though significant elimination of BPA can occur during wastewater treatment (mainly due to partial biodegradation during the wastewater treatment process) it is not complete, which supports the need for more effective treatment technologies to be applied in the future. BPA was also detected in sewage sludge samples, as it has the potential to adsorb to solid matrices.

Table 7: Summary of results of the screening of bisphenol A (BPA) in wastewater sample types

BPA	General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS	
detected/analysed	71/84	15/17	10/12	15/17	17/18	10/12	4/8	3/3	
% of detection	85	88	83	88	94	83	50	100	
Min - Max	(mg/L; SS:mg/kg dm)	10-34093	47-2539	24-4290	33-34093	10-2263	15-2962	197-481	0.23-3.82
Median		1116	743	1883	2620	273	775	112	1.50

In view of published data documenting the widespread occurrence of BPA the current screening results for BPA in wastewater and WWTPs are not surprising (Corrales et al., 2015). The presence of BPA in everyday consumer products and articles is reflected by its frequent detection in indoor dust. A U.S. meta-analysis showed that BPA occurs in rather high concentrations in indoor dust. Moreover, other hazardous substances such as phthalates were found to be present in highest concentrations and PFAS compounds in lowest concentrations (Mitro et al., 2016). Within the NonHazCity project BPA was detected in all dust samples collected from ten private residences in Stockholm (Giovanoulis, 2017). Through activities like floor-wiping and laundry part of the indoor load of BPA will be transferred to wastewater.

Stormwater has been identified as a relevant contributor of BPA transfer to the sewage system (Markiewicz et al., 2017). As with other hazardous substances found in outdoor dust, BPA may be transferred to stormwater because of its presence in the road and traffic environment (construction material, lubricants, car components, etc.).

With regard to the Baltic Sea one might expect a regular monitoring of BPA considering the permanent discharge of BPA from WWTPs and by other pathways. However, regular BPA monitoring data on concentrations in Baltic Sea environmental compartments including sediment or biota do not exist. Studies performed in the Gulf of Gdańsk revealed the accumulation of BPA in biota. For instance, this has been shown for a key species, the blue mussel (*M. trossulus*) which shows a seasonality of BPA levels with higher BPA concentrations in summer probably due to better solubility stimulated by higher water temperature (Staniszewska et al., 2017).

A Swedish chemical screening study detected BPA in muscle samples of Baltic Sea fish including herring, flounder and perch from almost all sampling sites (Lilja et al., 2009). Another Swedish study showed that BPA is present in fish muscle at roughly equal levels in inland waters and at marine sites (WSP environmental, 2007).

3.5 Perfluoralkyl Substances (PFAS)

Perfluoralkyl substances (PFAS) are a large group of hazardous substances with a widespread use in commercial products and industrial applications. PFAS are of global concern because of their persistence, bioaccumulation and possible adverse effects on biota. PFAS have fat and water repellent properties as well as being highly temperature resistant. Although the use of PFAS has decreased people can still be exposed to PFAS because they do not break down easily and are still present in the environment (Ahrens & Bundschuh, 2014).

The most prominent representatives of PFAS chemicals are perfluorooctane sulphonate (PFOS) and perfluoro octanoic acid (PFOA) which are considered as sentinel substances due to their worldwide high content in environmental samples.

Typical sources for PFAS in the environment are, landfills, and fire training sites as well as diffuse sources such as households and atmospheric deposition.

PFAS persist in humans and biota for long periods of time and may accumulate to levels where adverse health effects occur. For example, it has been suggested that the consumption of contaminated fish from the Baltic Sea contributes significantly to human blood levels of PFAS (Falandysz et al., 2006).

Exposure of humans to low levels of PFAS occurs through food, which also can become contaminated with PFAS through food packaging. Exposure can also happen during the normal use, biodegradation or disposal of consumer products that contain PFAS such as non-stick cookware, water repellent outdoor textiles and paper and packaging materials and carpets. Since PFAS adsorb to dust particles indoor dust is a major exposure route as well.

PFOS has been produced and used since the 1950s. Although its production is reduced or even phased out it is still considered a ubiquitous environmental contaminant. It is an EDC which has been shown to disturb the immune system as well as causing developmental and reproductive disorders (EDC).

As one of the major PFAS representatives PFOS is affected by environmental and health policy regulations. In 2009 PFOS was added to Annex B of the Stockholm Convention on POPs. Other EU legislation is also focused on PFOS and its derivatives. PFOS is classified under REACH as PBT substance and has been added to the WFD list of priority substances as amended in the WFD daughter directive on EQS (EQSD 2013/39/EU). PFOS is also included in the HELCOM list of substances or substance groups of specific concern to the Baltic Sea which was adopted as part of the Baltic Sea Action Plan (BSAP). Furthermore, PFOS is one of the HELCOM core indicators of hazardous substances. Since June 2011 the use of legacy firefighting-foam products containing >0.001wt% PFOS has been banned in the EU. Another PFAS representative, PFOA and its ammonium salt (APFO) are listed as SVHC in the REACH candidate list. It is noteworthy that a recent Swedish survey on PFAS in surface waters revealed that less than 5% of the identified PFAS compounds are covered by some form of EU regulation (Fischer et al., 2016).

The results of the screening analysis of PFAS substances in wastewater and WWTP samples from pilot municipalities are summarized in **Table 8**. PFBA was found more frequently in industrial and SME wastewater samples than stormwater or WWTP influent samples, and was not detected in samples from residential areas. Maximum detected concentrations were more than ten times the detection limit.

PFBS was more frequently detected in stormwater samples than in other sample types. It was not detected in either residential or wastewater effluent samples or in sediments. Maximum detected concentrations were approximately ten times the detection limit.

PFDS was not detected in any samples.

PFHPa was detected in more than half the stormwater samples and all sediment samples. The compound was detected in a minority of samples from all other environments, except residential areas where it was not detected. The maximum detected concentrations were approximately fifty times the detection limit.

PFHXa was only detected in sediment, wastewater influent and effluent. Maximum reported concentrations were approximately 150 times the detection limit.

Both linear and branched forms of PFHxS were detected. In general, linear forms were detected more frequently, being present in all of the WWTP effluent samples and approximately three quarters of the influent samples. Maximum reported concentrations were close to 800 times the detection limit.

Table 8: Summary of results of the screening of target perfluoralkyl substances (PFAS) in analysed sample types

PFAS	General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
PFBA (perfluorobutanoate)								
detected/analysed	17/92	0/19	4/12	7/20	1/18	2/14	3/9	2/4
% of detection	18	0	33	35	6	14	33	50
Min - Max	(ng/L; SS: 3.4-55	<3.4	<3.4-36	<3.4-55	<3.4-12	<3.4-13	<3.4-21	<1.8-27
Median	(ng/g ww) <3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	11

PFAS	General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
PFBS (perfluorobutane sulfonate)								
detected/analysed	14/92	0/19	2/12	1/20	5/18	4/14	2/9	0/4
% of detection	15	0	17	5	28	29	22	0
Min - Max (ng/L; SS: ng/g ww)	<0.205-2.1	<0.21	<0.21-1.6	<0.21-1.0	<0.21-1.7	<0.21-2.1	<0.2-1.31	<0.12
Median	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.12
PFDS (perfluorodecane sulfonate)								
detected/analysed	0/92	0/19	0/12	0/20	0/18	0/14	0/9	0/4
% of detection	0	0	0	0	0	0	0	0
Min - Max (ng/L; SS: ng/g ww)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.005
Median	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.005
PFHpA (perfluoroheptanoate)								
detected/analysed	24/92	1/19	2/12	3/20	8/18	4/14	6/9	4/4
% of detection	26	5	17	15	44	43	44	100
Min - Max (ng/L; SS: ng/g ww)	<0.04-2.3	<0.04-0.32	<0.04-1.2	<0.04-0.28	<0.04-0.85	<0.04-0.92	<0.04-2.3	0.067-0.52
Median	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.28
PFHxA (perfluorohexanoate)								
detected/analysed	5/92	0/19	0/12	0/20	0/18	2/14	3/9	3/4
% of detection	5	0	0	0	0	19	50	75
Min - Max (ng/L; SS: ng/g ww)	<0.04-6.8	<0.04	<0.04	<0.04	<0.04	<0.04-3.7	<0.04-6.8	<0.11-2.2
Median	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	1.9
PFHxS (branched) (perfluorohexane sulfonate)								
detected/analysed	32/92	8/19	5/12	3/20	5/18	9/14	2/9	1/4
% of detection	35	42	42	15	28	64	22	25
Min - Max (ng/L; SS: ng/g ww)	<0.04-5.1	<0.04-1.9	<0.04-4.6	<0.04-5.1	<0.04-0.65	<0.04-2.0	<0.04-0.2	<0.005-1.1
Median	<0.04	<0.04	<0.04	<0.04	<0.04	0.57	<0.04	<0.005
PFHxS (linear) (perfluorohexane sulfonate)								
detected/analysed	51/92	12/19	7/12	6/20	8/18	11/14	7/9	2/4
% of detection	55	63	50	35	44	78	79	50
Min - Max (ng/L; SS: ng/g ww)	<0.04-31	<0.04-4.6	<0.04-31	<0.04-8.6	<0.04-4.2	<0.04-3.0	<0.15-2.8	<0.02-0.85
Median	0.89	0.86	0.45	<0.04	<0.04	0.92	0.33	0.028
PFOA (perfluorooctanoate)								
detected/analysed	64/92	13/19	9/12	11/20	9/18	13/14	9/9	4/4
% of detection	70	68	75	55	50	93	100	100
Min - Max (ng/L; SS: ng/g ww)	<0.04-65	<0.04-1.3	<0.04-2.7	<0.04-7.6	<0.04-65	<0.04-15	0.59-1.7	0.073-0.75
Median	0.53	0.22	0.49	0.11	0.063	0.77	1.0	0.42
PFOS (branched) (perfluorooctane sulfonate)								
detected/analysed	37/92	5/19	5/12	3/20	8/18	5/9	11/14	1/4
% of detection	40	26	42	15	44	79	56	25

PFAS		General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
Min - Max	(ng/L; SS: ng/g ww)	<0.04-11	<0.04-6.3	<0.04-11	<0.04-0.52	<0.04-2.2	<0.04-1.7	<0.04-1.8	<0.010-0.19
Median		0.135	<0.04	<0.04	<0.04	<0.04	0.71	0.35	<0.010
PFOS (linear) (perfluorooctane sulfonate)									
detected/analysed		45/92	5/19	5/12	5/20	11/18	11/14	8/9	2/4
% of detection		49	26	42	25	61	79	89	50
Min - Max	(ng/L; SS: ng/g ww)	<0.04-22	<0.04-13	<0.04-22	<0.04-0.62	<0.04-6.4	<0.04-1.6	<0.04-2.7	<0.010-1.6
Median		0.18	<0.04	<0.04	<0.04	0.35	0.50	0.38	0.15

PFOA was detected in most samples. The substance was present in all WWTP effluent and sludge samples and more than 90% of the WWTP influents sampled. Maximum detected concentrations were approximately 1500 times the detection limit.

Both linear and branched forms of PFOS were detected, with a slightly higher frequency for the linear forms. The highest detection frequencies were in WWTP effluent samples. The maximum detected concentrations were approximately 500 times the detection limit.

As is shown in **Figure 4**, the majority of the perfluoralkyl substances analysed were present in wastewater samples from five to six municipalities. PFHxA which was only detected in three municipalities showed also the lowest detection frequency with regard to all samples analysed. PFHxS (linear), PFOA and PFOS (branched, linear) were the substances most often detected in wastewater samples.

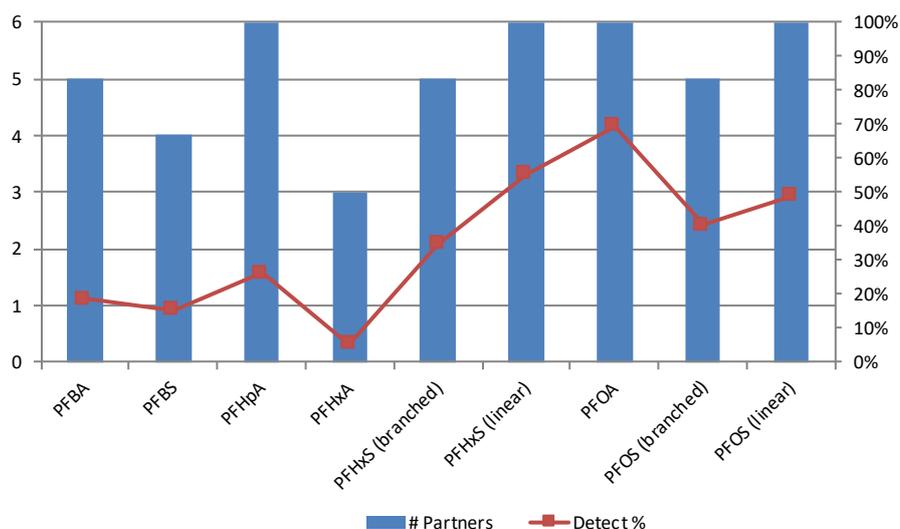


Figure 4: Number of municipalities where perfluoralkyl substances were found in sewage water (# Partners) and the overall detection frequency (Detect %). (for full names of substances see Table 8)

Due to their frequent presence in consumer products and articles, and in combination with their extraordinary high persistency PFAS are continuously emitted to domestic wastewater. This is confirmed by the current PFAS screening, where several PFAS compounds were detected less or more frequently in wastewater samples from residential areas. The relatively high detection frequencies of PFOA and PFOS support the fact that both compounds are usually among the most abundant PFAS in raw wastewater.

The analysis of PFAS in wastewater from a residential area in Stockholm revealed concentrations of e.g. PFBA, PFOA and PFOS to be below the respective detection limits (<10 - <17 ng/L). This is similar to the PFAS concentrations determined in the current screening study in wastewater samples from residential areas of pilot municipalities.

The stormwater samples showed relatively high concentrations of PFAS, which is consistent with published data. For example, in a study on PFAS in stormwater from different urban areas PFAS were

found in 100% of stormwater runoff samples. PFAS from stormwater runoff in residential areas was mainly due to rainfall, whereas PFAS sources at both commercial and industrial areas contributed to the atmospheric deposition (Xiao et al., 2012).

Since WWTP collect all PFAS released to the sewage system, they are a significant pathway for PFAS emissions to the aquatic environment. In general, PFAS are only poorly removed by the treatment processes commonly used in WWTPs. The fate of 10 PFAS compounds were analysed in influent and effluent wastewater and in sludge samples by Guo et al. (2010) who showed that PFOS was dominant in sludge samples, whereas PFOA was dominant in wastewater. The PFOS loads tended to decrease during treatment in most tested WWTPs, whereas PFOA levels increased (Guo et al., 2010).

In a mass balance calculation of PFAS in the Baltic Sea it was concluded that WWTP effluents are responsible for <5% of the total PFAS input and that by far the greatest contribution is atmospheric deposition (Filipovic et al., 2013). PFAS compounds are considered as relevant hazardous substances in the Baltic Sea, as the proxy PFOS has been included in the HELCOM list of substances of specific concern to the Baltic Sea. Furthermore, PFOS is one of the HELCOM core indicators.

During a screening of hazardous substances in the Eastern Baltic PFOS has been detected in liver samples of herring, flounder and perch whereas other PFAS compounds were mostly below detection limits (Lilja et al., 2009). PFAS are also present in sea birds e.g. the guillemot (*Uria aalge*). PFOS was the dominant compound observed in adult and chick liver and in eggs (Holmström & Berger, 2008). Overall PFOS has been observed in all levels of the Baltic Sea food web with marine mammals having considerably higher contaminant levels compared to marine fish. The major area of concern for PFOS is the secondary poisoning of top predators, such as seals and predatory birds (HELCOM, 2010).

Yearly monitoring of PFAS in Mälaren and some smaller lakes in the Stockholm region shows widespread occurrence of for example PFOS, PFOA, PFHxS and PFHxA in surface water and PFOS and perfluorodecanoic acid (PFDA) in perch. The yearly average levels of PFOS in surface water ranges from 0.66 to 46 ng/L and the levels of PFOS in perch muscle ranges from 1.1 to 51 ng/g fresh weight. (Stockholms miljöbarometer, 2018).

3.6 Pharmaceuticals

The contamination of water with pharmaceuticals is a growing environmental problem. Many pharmaceuticals consumed by humans and animals are not metabolised and they reach surface waters either directly or via the sewage system. As a result pharmaceuticals represent a major group of emerging pollutants in marine and coastal waters (aus der Beek et al., 2016).

The most commonly detected pharmaceuticals include antibiotics, analgesics and estrogens. Among the analgetics the anti-inflammatory drug diclofenac is one of the most frequently detected pharmaceuticals in environmental samples worldwide. It is used externally and internally with the majority of ingested diclofenac excreted unchanged to wastewater. In WWTPs, diclofenac is only eliminated to a rather small extent. Therefore, it is regarded as a suitable indicator of residential wastewater inputs to the aquatic environment (Hillenbrand et al., 2014)

In addition to diclofenac, the estrogenic hormones 17 β -estradiol and 17 α -ethinylestradiol were chosen as target substances, since they are also known to have widespread occurrence in the environment. Excess 17 β -estradiol and 17 α -ethinylestradiol are excreted via urine as water-soluble conjugates and either enter the aquatic environment directly (veterinary pharmaceuticals) or, due to their incomplete removal, via WWTPs (human use). The main source of the hormone 17 β -estradiol is from natural human production, but is also linked with hormonal replacement therapies, whereas the synthetic hormone 17 α -ethinylestradiol is most frequently used as the estrogen component of oral contraceptives.

Endocrine-active pharmaceuticals including 17 β -estradiol and 17 α -ethinylestradiol can cause adverse effects on aquatic animals at very low concentrations. The toxicological impact can include reproductive disorders, behavioural changes and population relevant effects (Aris et al., 2014).

The policy relevance of this class of compounds in the Baltic Sea environment is underpinned by the 2010 and 2013 HELCOM Ministerial Declarations where contracting parties agreed to collect and assess data about the presence of pharmaceuticals in the aquatic environment (UNESCO & HELCOM, 2017). To this end, diclofenac, 17 β -estradiol and 17 α -ethinylestradiol were included in the set of HELCOM core indicators for monitoring of hazardous substances (HELCOM, 2013). Furthermore, the EU Strategy for the Baltic Sea Region (EUBSR) Policy Area Hazards has selected the topic of pharmaceuticals in

the Baltic environment during the years 2015-2017. At the EU level diclofenac, 17 β -estradiol and 17 α -ethinylestradiol were included in the first watch list of priority substances to be monitored across the EU as mandated by Directive 2013/39/EU.

It is well known that both analgesics such as diclofenac and estrogens used for medication are present in the effluent of WWTPs. However, data analysed in samples collected upstream of WWTPs in the sewage system are scarce.

In **Table 9** the results of the screening of pharmaceuticals are presented as descriptive statistic values of measured concentrations and as detection frequencies.

Median concentrations of diclofenac differed between the sample types, with the highest values observed for wastewater taken from WWTP influents (346 ng/L) and effluents (302 ng/L). Upstream of WWTPs, the median concentration of diclofenac was much lower, ranging from 6 to 191 ng/L. The highest concentration was noted for residential areas - 1502 ng/L; a similar level was observed in WWTP influents. This can suggest that residential areas are significant sources of diclofenac present in WWTPs. In addition, diclofenac was found in one sample taken from a hospital. The highest detection frequency was observed for residential areas (35%) and WWTP influents (58%) and effluents (50%). Diclofenac was also detected in one sludge sample.

Detection frequencies for 17 β -estradiol were generally low. It was found in only one residential and one industrial area sample. This low detection frequency is likely due to the use of an analytical method with a relatively high detection limit (**Table 9**). Detection frequencies of 17 α -ethinylestradiol was low to moderate. The highest frequency was noted for residential wastewater and WWTP influents, 41% and 58%, respectively. Similar results were noted for diclofenac. The highest median concentrations of 17 α -ethinylestradiol were noted in wastewaters taken from residential areas and WWTP wastewaters. The highest concentrations were determined in residential areas samples and WWTP influents. This means that the 17 α -ethinylestradiol present in WWTP is likely to be directly related to human consumption. The reason for this is that 17 α -ethinylestradiol is used as the main component of contraceptive pills. The median concentrations of 17 α -ethinylestradiol in WWTP influents and effluents were similar. This suggests that currently applied technologies do not successfully remove 17 α -ethinylestradiol. As a consequence, 17 α -ethinylestradiol is released into recipient waters including the Baltic Sea.

Table 9: Summary of results of the screening of target pharmaceuticals in wastewater sample types Wastewater from residential area (RA), stormwater (SW), sewage water from industrial areas (IA), small and medium-sized enterprises effluents (SME), influent sewage water (ISW), effluent sewage water (ESW), sewage sludge (SS)

Pharmaceuticals	General presence in water samples	RA	IA	SME	SW	WWTP-ISW	WWTP-ESW	SS
Diclofenac (DIC)								
detected/analysed	23/84	6/17	1/12	2/17	3/18	7/12	4/8	1/3
% of detection	27	35	8	12	21	58	50	33
Min - Max (ng/L; SS:ng/kg dm)	21-1505	23-1502	52	36-296	44-680	21-1505	36-1229	0.25
Median	174	191	6	21	8	346	302	0.25
17 β -Estradiol (E2)								
detected/analysed	2/84	1/17	1/12	0/17	0/18	0/12	0/8	0/3
% of detection	2	6	8	0	0	0	0	0
Min - Max (ng/L; SS:ng/kg dm)	46-82	46	82	0	0	0	0	0
Median	64	4	8	0	0	0	0	0
17 α -Ethinylestradiol (EE2)								
detected/analysed	19/84	7/17	1/12	2/17	0/18	7/12	2/8	1/3
% of detection	23	41	8	12	0	58	25	33
Min - Max (ng/L; SS:ng/kg dm)	65-1863	65-1863	399	553-668	0	103-1565	150-1270	10.16
Median	212	274	34	73	0	286	178	10.16

An overall detection frequency of <30% was observed for the target pharmaceuticals (**Figure 5**). Similar results were obtained in bigger cities (Gdańsk, Riga, Kaunas) and smaller (Pärnu, Šilalė) municipalities. Diclofenac and 17 α -ethinylestradiol were detected in wastewater samples from each municipality, whereas 17 β -estradiol was detected in samples from only two municipalities. As mentioned above, the low detection frequency of steroid hormones is likely due to the use of an analytical method with a relatively high detection limit.

Target pharmaceuticals were found mainly in wastewater originating from residential areas (Table 9). From such diffuse sources, pharmaceuticals are transferred to WWTPs, where they will be more or less degraded or transformed and released to the environment with effluent water or sludge.

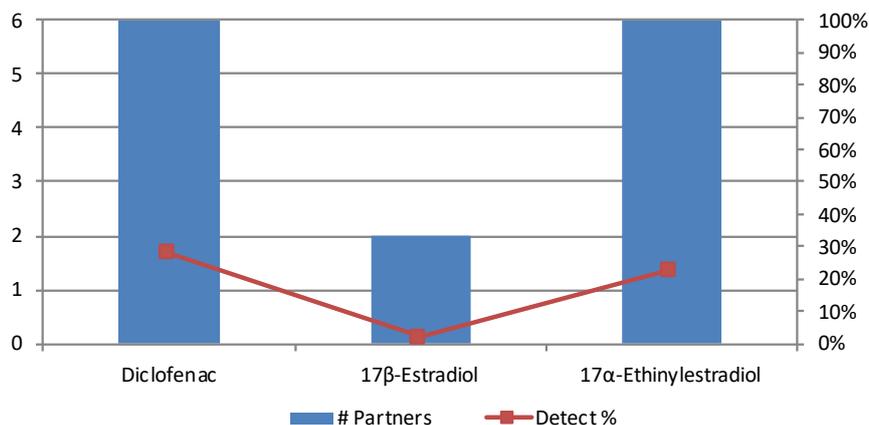


Figure 5: Number of municipalities where pharmaceuticals were found in sewage water (# Partners) and the overall detection frequency (Detect %).

The frequent detection of diclofenac in wastewater samples reflects the abundant use of this pharmaceutical, which is one of the 20 most sold pharmaceuticals in the Baltic Sea catchment area (UNESCO and HELCOM, 2017). Diclofenac is also among the 20 pharmaceuticals with the highest concentrations in the influent and effluent of WWTPs and with only very low levels of removal during conventional wastewater treatment. Not surprisingly, it is one of the most frequently detected pharmaceuticals in recipient waters and the Baltic Sea (UNESCO and HELCOM, 2017). On the other hand, the availability of data is still scarce if compared to routinely monitored hazardous substances (UNESCO and HELCOM, 2017). However, one can presume that monitoring of diclofenac and estrogens in the Baltic Sea catchment area will improve, since EU member states have been required to monitor these pharmaceuticals as part of the Water Framework Directive watch list.

In effluent wastewater from three Swedish WWTPs, in Stockholm, Västerås and Uppsala, the concentrations of diclofenac ranged from 59 -688 ng/L, <DL – 592 ng/L and 309 – 1776 ng/L. The corresponding average concentrations were 287 ng/L, 200 ng/L and 690 ng/L (Kårelid et al. 2017). These diclofenac concentrations are of the same levels as those observed in the current pilot study.

Data regarding levels and effects of diclofenac and other pharmaceuticals in Baltic Sea biota is at present limited. A few studies exist on effects of certain pharmaceuticals on organisms from the Baltic Sea including blue mussel, amphipod crustaceans and algae. Diclofenac bioaccumulates in the blue mussel (*Mytilus trossulus*) and has been shown to have negative physiological effects in laboratory experiments (Ericson et al., 2010).

Estrogens may cause reproductive disorders as has been shown with Baltic Sea eelpout (*Zoarces viviparus*). The exposure of this viviparous fish species to environmentally occurring levels of estrogens during the early stages of pregnancy caused severe fry malformation (Morthorst et al., 2016). In male eelpout E2 led to a marked pathology of the testis and induced the synthesis of the female yolk precursor vitellogenin (Christiansen et al., 1998).

Ethinylestradiol and estradiol were identified in effluent water from a Swedish WWTP receiving mainly domestic wastewater, ethinylestradiol exceeded levels shown to be estrogenic to fish by 45 times. The estrogenicity of the effluent water was investigated by introducing juvenile rainbow trout (*Oncorhynchus mykiss*) in cages downstream of the WWTP. After 2 weeks, estrogens were present in the bile of the fish, and vitellogenin was found in large amounts in the plasma (Larsson et al., 1999).

The analysis of the samples taken from WWTP influents and effluents showed that conventional wastewater treatment technology is not able to remove pharmaceuticals completely from municipal wastewater. This confirms well known findings about the overall degradation and removal of pharmaceuticals in conventional WWTPs.

In this context the adsorption of pharmaceuticals to sewage sludge is a potentially serious problem if the sludge is used as a soil amendment (Berthod et.al, 2017). Sludge application may transfer pharmaceuticals to agricultural and other soils with negative consequences for microbial and faunal activity.

Since pharmaceuticals are needed for maintaining human and animal health, it is more difficult to reduce their use or find substitutes than is the case with other hazardous substances. However, source related measures that minimize the occurrence of pharmaceuticals in wastewater are urgently needed considering the poor removal efficiencies of many pharmaceuticals in conventional WWTPs and the potential for pharmaceuticals to have undesirable effects in the environment.

3.7 Local priority substances

Local priority hazardous substances are substances and substance groups that are particularly environmentally important in a specific municipality or region. Ideally, emission reduction actions performed in the municipality should be based on the list of local priority substances and their identified sources. Since there are significant local knowledge gaps concerning the relevance of different sources, this is not always possible, but rather, measures are selected more pragmatically based on the possibilities for municipalities to influence the use of hazardous substances. Still, the list of local priority substances can serve to identify hazardous substances for which actions are needed, even if the actions taken are not specifically directed towards them.

In the selection process for local priority hazardous substances the following criteria were used:

- The substance is harmful to health and the environment
- The substance is present in the municipal water environment (wastewater, sludge, stormwater, sediment or surface water)
- The municipality has knowledge about local sources of the substance
- There are possibilities for the municipality to take measures to reduce emissions of the substance

The screening activities performed within the NonHazCity project have given all partner municipalities information on occurrence and concentration ranges of selected hazardous substances in their wastewater, stormwater and in some cases sewage sludge. This information has been a valuable input to the process of identifying local priority hazardous substances (**Table 10**).

Table 10: Local priority substances in the partner municipalities identified within the project. Substances/substance groups for which Local Substance Source Maps were elaborated are marked in bold.

Municipality	Priority substances		
Stockholm	Alkylphenols and their ethoxylates (AP, APE)	Brominated flame retardants (BFR)	Cadmium (Cd)
	Phthalates (DEHP, DINP etc.)	Bisphenols	Lead (Pb)
	Perfluoralkyl substances (PFAS)	Tributyltin (TBT)	Copper (Cu)
	Chlorinated paraffins (SCCP, MCCP, LCCP)	Anti-bacterial substances (e.g. silver, triclosan)	Zinc (Zn)
Turku	Alkylphenols and their ethoxylates (AP, APE)	Brominated flame retardants (BFR)	Chromium (Cr)
	Phthalates	Bisphenols	Tributyltin (TBT)
	Perfluoralkyl substances (PFAS)	Copper (Cu)	
Gdansk	Alkylphenols and their ethoxylates (AP, APE)	Polycyclic aromatic hydrocarbons (PAH)	Cadmium (Cd)
	Phthalates	Bisphenols	

Municipality	Priority substances		
Pärnu	Alkylphenols and their ethoxylates (AP, APE)	Phthalates	Bisphenols
Rīga	Alkylphenols and their ethoxylates (AP, APE)	Bisphenols	Diclofenac
Kaunas	Alkylphenols and their ethoxylates (AP, APE)	Bisphenols	Phthalates
Šilalē	Alkylphenols and their ethoxylates (AP, APE)	Bisphenols	Phthalates

From the list of local priority substances, each partner municipality has identified one or more substances or substance groups for which source tracking was performed and local substance source maps were elaborated.

4 SOURCE MAPPING OF LOCAL PRIORITY HAZARDOUS SUBSTANCES

4.1 Method

Source mappings were based on Substance Flow Analyses (SFA). The outputs of SFA quantify the stocks and flows of a chemical or group of chemicals within a defined system (usually a geographic region) during a specified time period (usually a year) (Jonsson et al. 2008). The SFA includes inflows to the system (e.g. import and production), emissions to the environment and other outflows to recipients outside the system (such as exports of products or waste). Sometimes SFA also include the environmental distribution of a substance.

Due primarily to data limitations, complete SFA were not elaborated within the NonHazCity project, but instead simplified “Substance Source Maps” were created. These Substance Source Maps were used to assess the quantities and emission pathways of local priority hazardous substances (Chapter 3.7) within the pilot municipalities. The work focused on identification of emission sources, outflows and the environmental distribution of emissions to the urban water cycle and the surface water recipients. The timeframe was one year and the geographic region was defined by the borders of the municipality.

The emission string concept

The knowledge about sources of emissions can be described and codified using “emission strings” (Holten Lützhøft et al., 2012; Andersson et al., 2012a; Andersson et al., 2012b). In short, an emission string describes an emission source by identifying the particular substance being emitted (CAS #), the (economic) activity resulting in the emission, the specific emission process during which the substance is released, the emission factor and the receiving compartments. To quantify the emissions, knowledge about emission factors or other quantitative release data are included as well as an “emission factor multiplier” that quantifies measurable factors to which emissions are related (e.g., number of inhabitants, traffic load, number of dentists, number of km² gardens, etc.) Additional information about the environmental compartments to which emissions are distributed (i.e. air, water, soil etc.) and the fractions of emissions to each compartment are also compiled.

Identification and quantification of emission sources

Relevant emission sources for a Local Substance Source Map were identified by crosschecking existing emission string tables (from the previous EU-funded ScorePP and COHIBA projects) for the chosen substances with local information on what activities are represented in the municipality. This was supplemented with information from e.g. national environmental/chemical authorities and their registers, regional business organisations with knowledge of industrial use, importing industries, scientific literature, national/regional investigations, and national official statistics.

For substances where emission string tables were not available, compilation of relevant emission sources and emission factors was performed with the help of local and national information, general information from the literature and other available documents including EU Risk Assessment Reports.

Substance Source Maps

The emission string table assembles and structures information about the sources with their associated emission factors and emission factor multipliers. Substance loads from each source are given as the product of the emission factor and the emission factor multiplier. The percentage estimate provides information on the distribution of emissions to different environmental compartments. All this information is presented in a substance source map which describes how the different emission sources are interconnected.

4.2 Local Substance Source Maps

The NonHazCity pilot municipalities participating in the source tracking were Stockholm (Sweden), Turku (Finland), Pärnu (Estonia), Riga (Latvia), Kaunas region (Lithuania), Šilalė (Lithuania) and Gdańsk (Poland). Local Substance Source Maps were elaborated for four different substances/substance groups.

It is important to note that the Local Substance Source Maps are based on available information. Several emission factors are missing, or are very uncertain. Furthermore, several assumptions based on expert judgement have been made in the attempts to quantify the emissions.

Nonylphenols and their ethoxylates (NP and NPE)

Source maps for nonylphenols (NP) and their ethoxylates (NPE) were elaborated for Riga, Šilalė, Kaunas district and Gdańsk.

Degradation of NPE in WWTPs or in the environment generates the more persistent NP. Thus NPE sources are also possible sources of NP and this is why emissions reported here are a combination of NP and NPE.

As none of the cities have any large industry emitting NP or NPE, the results were similar. Diffuse sources were the most important (Chapter 3). Washing of textiles and use of cosmetics, hygienic products and detergents were assessed to be the most important sources for emissions of NPs and their ethoxylates to wastewater. Runoff from buildings (from NP/NPE in concrete, adhesives, paints etc.) and emissions from vehicles were also determined to be important sources for emissions to stormwater (**Figure 6**).

The estimated emissions from washing of textiles were based on a relatively uncertain emission factor obtained from a 2008 Swedish study and calculated assuming that NP is released every time a household washes imported textiles, resulting in an emission factor of 2.1 g/inhabitant/year to wastewater (Prevodnik et al, 2008). However, in 2015 extended restrictions on imports of clothing and other textile products containing NPE were adopted by the European Commission. This restriction may already have had an impact, potentially leading to lower emissions of NPE to wastewaters within the EU. Therefore, the estimated yearly load of NPs and their ethoxylates to wastewater may be overestimated, as the emission factor used is from 2008.

Semi-conceptual Source Map for Nonylphenols and their ethoxylates

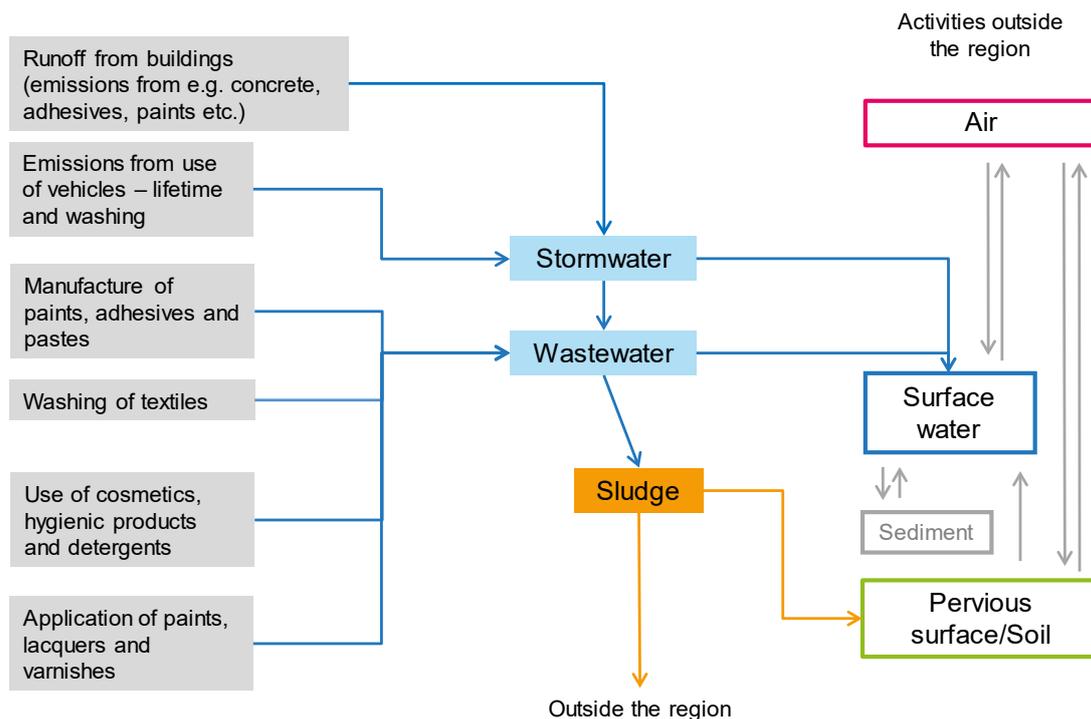


Figure 6: Semi-conceptual Local Substance Source Map for NP and NPE showing emission sources identified in more than one of the cities. A Source Map most often includes loads (kg/year) from each source and pathway. This semi-conceptual Source Map does not show any loads, only identified sources and pathways, and is not representative of any specific city.

In WWTPs, NPEs are to a large extent degraded to NPs, which in many cases are shown to be mainly distributed to the sewage sludge. Therefore, only a minor proportion of the emissions of NPs and their ethoxylates are distributed to surface waters. However, still considerable amounts of NPs and their ethoxylates are emitted to surface waters from WWTPs (Chapter 3.3).

Phthalates

Source maps for phthalates were elaborated for Stockholm, Pärnu and Gdańsk. Stockholm focused on source tracking of diisononyl phthalate (DINP), Gdańsk focused on di(ethylhexyl)phthalate (DEHP), while Pärnu elaborated a source map for phthalates in general. Similar sources are presented in the three different source maps.

DEHP is identified as a substance of very high concern (SVHC) in the EU REACH regulations and included on the Candidate list, and is also on the Authorisation list, Annex XIV, in REACH and in the WFD list of priority hazardous substances. Because of these regulations, DEHP has started to be phased out and is often replaced by DINP, so it is not surprising that the sources are similar.

Figure 7 shows a semi conceptual example of a Local Substance Source Map for phthalates.

Semi-conceptual Source Map for Phthalates

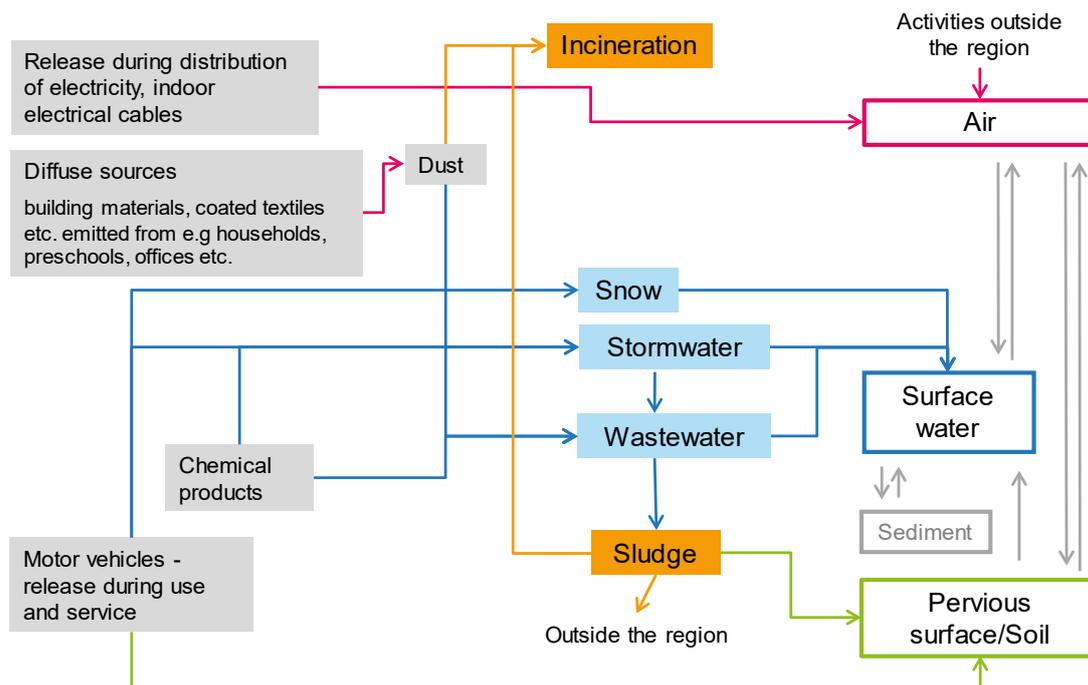


Figure 7: Semi-conceptual example of a Local Substance Source Map for phthalates showing emission sources identified in more than one of the cities. This semi-conceptual Source Map does not show any loads, only identified sources and pathways, and is not representative of any specific city.

Diffuse sources including emissions from articles and materials used in e.g. households, preschools and offices are assessed to be important sources. Cars and other motor vehicles, as well as motor vehicle services such as car washes are also estimated to be important sources. Furthermore, use of chemical products, both by households and enterprises is estimated to be an important source for emissions of phthalates to wastewater.

The major part of the emissions of phthalates is distributed to wastewater and stormwater, and further to surface water and sewage sludge. However, indoor emissions are likely to be adsorbed to dust to a large extent, and are therefore probably distributed to waste as well and then in many cases incinerated.

Perfluoralkyl substances (PFAS)

A source map for one PFAS, perfluorooctane sulfonate (PFOS), was elaborated for Turku.

It has been estimated that the release from contaminated soils is one of the most significant sources of PFOS to the aquatic environment (Mehtonen et al 2016). PFOS contamination in soils in Turku could originate e.g. from the use of firefighting foams in training areas or fire sites, ski waxes, use of municipal sludge in plantations, atmospheric deposition, etc. As there is no data on soil stocks of PFOS in Turku, no load could be calculated for this source.

Diffuse sources of PFOS include industrial use, as well as releases from stocks of impregnated textiles and other consumer products. At the scale of this study (Turku city), the emissions are very uncertain, and no attempts have been made to define emission factors for each separate source. The estimated total yearly load is 300-600 kg to wastewater, based on the results from the NonHazCity screening.

In addition to emissions from use of PFOS, certain other PFAS substances, such as perfluoroalkyl sulphonamides, fluoropolymers or some shorter chain PFAS can degrade into PFOS through photocatalysis or biodegradation (Mehtonen et al. 2016, Armitage et al 2009, Ahrens and Bundschuh 2014). This is also a source of PFOS to the aquatic environment to take in consideration.

Furthermore, atmospheric deposition of PFOS and related substances is a source of PFOS. Based on measurements from a pristine boreal catchment in Northern Sweden, approximately 400 km from Turku (Filipovic et al. 2015), and the average annual precipitation in Turku, the yearly load of PFOS from

atmospheric deposition is 8 kg. **Figure 8** shows a semi conceptual example of a Local Substance Source Map for PFOS.

Semi-conceptual Source Map for Perfluorooctanesulfonate (PFOS)

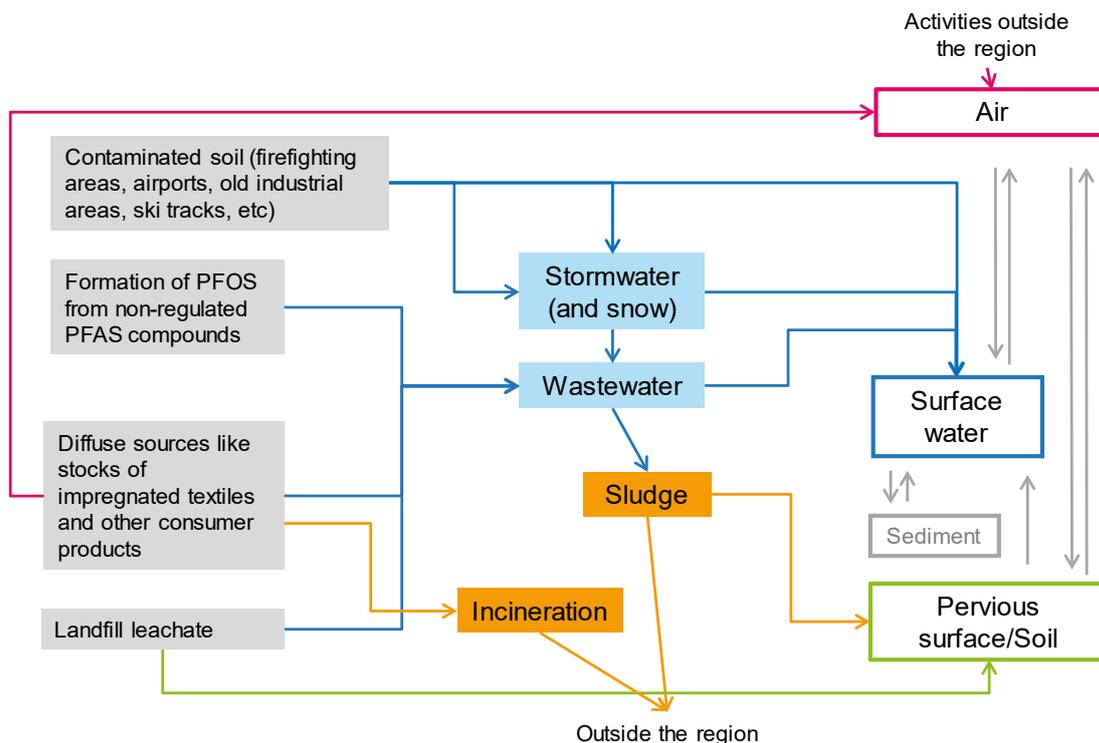


Figure 8: Semi-conceptual example of a Local Substance Source Map for perfluorooctanesulfonate (PFOS) showing emission sources identified in more than one of the cities. A Source Map most often include loads/year from each source and pathway. This semi-conceptual Source Map does not show any loads, only identified sources and pathways, and is not representative of any specific city.

Summary and Conclusions

Today, consumption-related diffuse sources are often more important emitters of hazardous substances than production-related point sources. This is supported by the results from the current source tracking performed within NonHazCity.

- Emissions from articles and materials used indoors in for example households, preschools, and offices are assessed to be important sources for all target substances. Emissions are mainly distributed via wastewater to surface water.
- Cars and other motor vehicles, as well as motor vehicle services such as car washes are estimated to be important sources nonylphenols and their ethoxylates as well as for phthalates. Emissions are distributed via stormwater and wastewater to surface water.

It is notable that there is still very little data available on the uses, emissions and environmental concentrations of organic hazardous substances on European and national levels, and even less data available on a municipal level. Thus, all of the analyses done are based on quite scarce data and are very rough estimates with a high degree of uncertainty. Furthermore, in some cities, for example in Turku and Stockholm, the wastewater treatment plant collects wastewater from several different municipalities in the region, hence, the municipal boundary is quite artificial when it comes to substance source tracking.

A municipality is geographically a very small entity which limits the application of the source mapping method. However, it can be concluded that local Substance Source Maps elaborated on a municipal level are useful tools for reducing emissions of priority hazardous substances and other pollutants from small scale emitters in urban areas. Substance Source Maps help to illustrate the flows and magnitudes of the substance of interest and they can be an important part of the toolkit for communicating hazardous substance risks in municipalities as well as for targeting, prioritisation and planning of reduction measures.

5 HAZARDOUS SUBSTANCES IN ARTICLES AND MATERIALS

To learn more about the content of hazardous substances in articles and materials, a range of indoor items were analysed for a suite of chemicals, with a focus on items commonly found in preschools.

New and old toys, hobby materials, mattresses and furniture from preschools in Stockholm were analysed for a range of harmful substances including phthalates, flame retardants, chlorinated paraffins, highly fluorinated substances and formamide. The purpose was to:

- investigate to what extent hazardous substances are found in articles and materials used in preschools, and thereby
- motivate preschools to dispose of articles that may contain hazardous substances, and
- check compliance of contracted suppliers with set criteria and legislation.

A total of 179 samples were analysed:

- 51 new items. These were newly purchased items from the city's contracted suppliers.
- 128 old items and materials. These were collected from preschools in Stockholm. Many of the old items analysed had previously been discarded by the preschools, as they have already started to work according to the City of Stockholm Chemicals Centre guidance document for a "Chemical Smart Preschool", developed as part of the city's chemicals action plan.

The articles and materials were collected and purchased during August-November 2016. The chemical analysis was performed by a contracted laboratory in November-December 2016 and in July 2017.

The study showed that many old articles contain high levels of hazardous substances. In many cases one or more of the analysed substances were detected above the levels permitted under current legislation (**Figure 9**). Hazardous substances were also found in new articles but at very low levels (**Figure 10**).

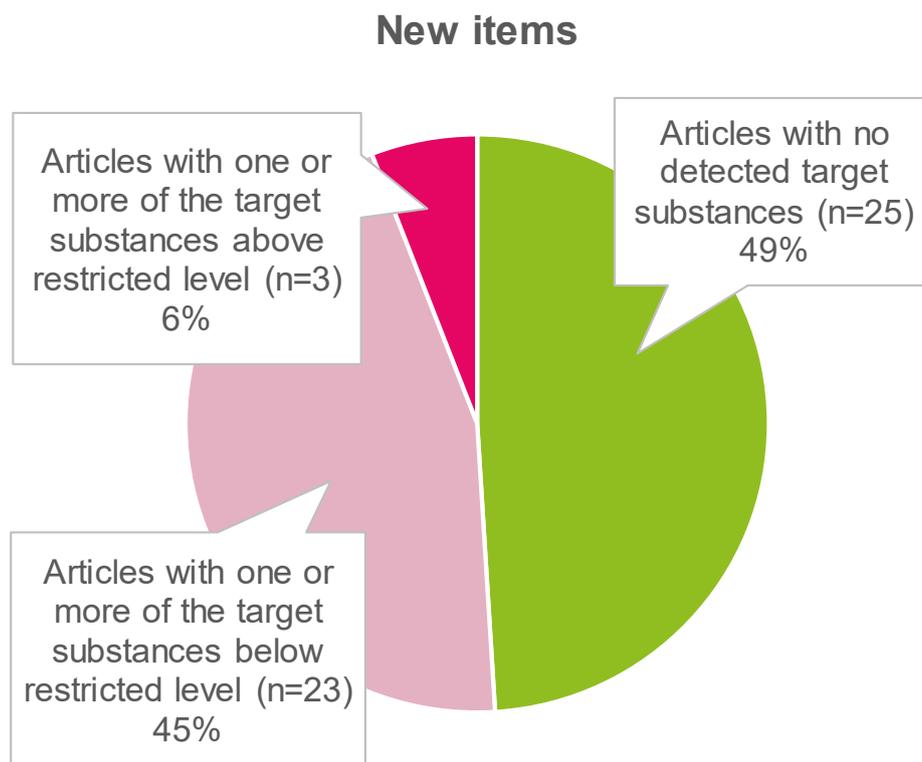


Figure 9: The distribution of old articles and materials containing quantifiable levels of any target substance above and below 1000 mg/kg (0.1% by weight), and no quantifiable levels, respectively.

concentrations up to 40% by weight in bags and other items used for dress up. Furthermore, chlorinated paraffins and very high levels of DEHP and DINP were found in a garden hose used for water play.

The high content of phthalates in many of the old items means that, according to current legislation, they would not be allowed on the market. In 62% of the old toys and childcare articles, at least one restricted phthalate was found at a level above the limit allowed by current legislation (0.1% by weight). For dress up clothes, furnishings and other non-toy items, 71% of the analyses showed levels above the current regulatory limit values. The items belonging to the latter group are not considered as toys or childcare articles, which means that, despite the high levels of phthalates, they would not be restricted in accordance with current legislation. Nevertheless, it is important to limit the exposure of these substances to children regardless of the type of goods they are present in.

A number of different types of highly fluorinated substances were analysed; for example, perfluorooctane sulfonate (e.g. PFOS), perfluoro carboxylic acids (PFCAs, e.g. PFOA) and fluorotelomer alcohols (FTOHs). Two FTOH substances were found in fabrics and mattress covers from suppliers of preschool articles (**Figure 12**). This may be due to the expected desire for good stain repellent properties of articles used in preschools. None of the analysed highly fluorinated substances were found in fabrics from office furniture suppliers.

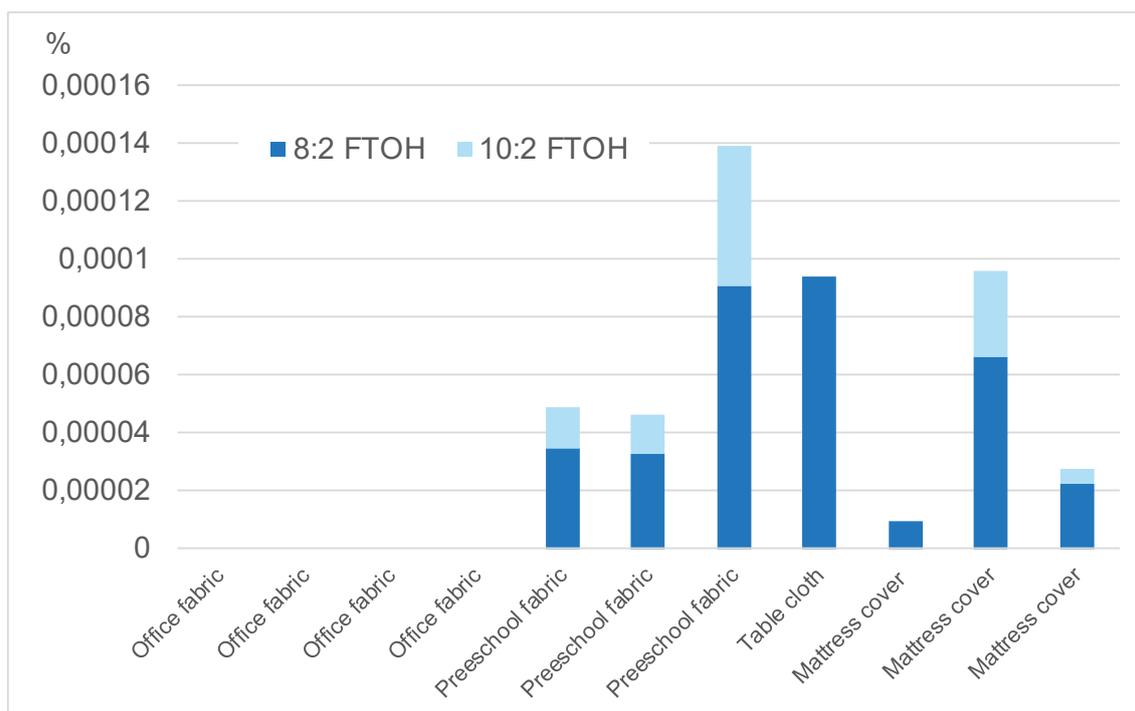


Figure 12: Total concentrations of the two most often detected PFAS substances (the fluorotelomer alcohols 8:2 FTOH and 10:2 FTOH) in new textile products.

Chlorinated phosphorous flame retardants were found in mattress foam, furnishings and toys. The highest concentrations were found for Tris(1,3-dichloroisopropyl)phosphate (TDCPP) and Tris(2-chloroethyl) phosphate (TCEP) in foam from old mattresses and old sofa cushions. None of the analysed brominated flame retardants were found in either old or newly purchased items, which is positive. Furthermore, the survey showed that new goods purchased from the municipality's procured product range are in most cases free from the harmful substances included in the survey.

Prohibited substances were, however, found in some of the new samples. This demonstrates the need for different aspects of green public procurement to be applied: first to include requirements concerning hazardous substances in tendering contracts, and second that the follow up of a procurement contract includes chemical analyses of substances that are regulated in legislation or in the procurement criteria.

6 SUMMARY AND RECOMMENDATIONS

The purpose of the pilot screening of hazardous substances and the source tracking carried out in partner municipalities of the project NonHazCity (“Innovative management solutions for minimizing emissions of hazardous substances from urban areas in the Baltic Sea Region”) was to investigate the presence of hazardous substances in samples of wastewater derived primarily from different urban emitters, stormwater and in samples from wastewater treatment plant (WWTP) influents and effluents. Local Substance Source Maps were elaborated to track back the potential sources of emissions of hazardous substances in the pilot municipalities. Furthermore, a range of indoor items used in preschools and offices were analysed for a suite of chemicals to learn more about the content of hazardous substances in everyday articles and materials.

The hazardous substances selected for analysis comprised pharmaceuticals, phthalates, alkylphenols, bisphenol A and perfluoralkyl substances (PFAS) and heavy metals. Some of the organic substances might be viewed as emerging pollutants, since they are usually not part of national freshwater and Baltic Sea monitoring programmes.

The overall finding from the screening survey is that the analysed substances were found in all types of samples in all pilot municipalities, meaning that these substances are widespread and originate from different types of diffuse sources in urban areas. There were no significant differences of hazardous substances levels between smaller and larger municipalities.

Although the findings are based on only one single pilot screening carried out in the NonHazCity partner municipalities, it is reasonable to assume that they in principle mirror the status of hazardous substances in the sewage system and WWTPs in other municipalities in the Baltic Sea catchment area.

Consumption-related diffuse sources are nowadays as important sources for hazardous substances than production-related point sources. This is confirmed by the results from the current source tracking performed within NonHazCity.

The following are some main findings:

- Concentrations of metals in effluent waters from WWTPs most often are within legally permitted levels.
- Phthalates, bisphenol A, alkylphenols and PFAS are the substance groups most frequently detected in all wastewater types, sewage sludge and stormwater.
- Alkylphenols and bisphenol A were detected in all types of samples. The highest levels of alkylphenols were found in wastewater from residential areas, while the highest levels of bisphenol A were observed in samples collected at points near industrial areas and small/medium enterprises.
- High concentrations of the pharmaceuticals diclofenac, 17 β -estradiol and 17 α -ethinyl-estradiol were found in domestic wastewaters and in influent and effluent water from WWTPs.
- WWTPs are potentially important pathways for release of hazardous substances to the Baltic Sea. Hazardous substances are emitted from upstream sources including articles and materials used in households, municipal sources and SMEs. These substances are incompletely removed during ordinary wastewater treatment and can enter the freshwater and marine environments.
- Households are an important source of hazardous substances. All of the analysed substances were detected in wastewater coming from residential areas, some of them in high concentrations. This indicates that consumer products and articles (materials present in households) are important sources of hazardous substances in the sewage system.
- Emissions from articles and materials used indoors in, e.g., households, preschools, offices are likely to be important sources for many of the target substances (nonylphenols and their ethoxylates, phthalates, PFAS,). Emissions are mainly distributed via wastewater to surface water.
- Many old articles found in preschools and elsewhere contain high levels of hazardous substances. Hence, it is important to sort out and dispose of for example old toys and materials in order to reduce the amount of hazardous substances present in the indoor environment.
- Even new articles and materials may contain unwanted and/or restricted substances, but much less frequently and often at lower concentrations than older ones. It is necessary to set up

procurement criteria which include chemical content, and it is important to check compliance with set criteria and legislation.

From these findings the following recommendations can be drawn:

- Measures targeting upstream sources must be used more widely in the effort to reduce emissions of hazardous substances into the Baltic Sea. The prioritization of sources and unwanted substances has to be done at all levels (local, regional, national and international) with a particular focus on the local municipal level.
- Better monitoring of legacy and emerging pollutants at all levels (local, regional, national and international) is needed to move effectively towards a hazardous substance-free environment.
- Targeting diffuse urban sources of hazardous substances should be a high priority for municipalities in the Baltic Sea Region.

What municipalities can do

In NonHazCity the local administrations are being approached to develop appropriate strategies to phase out hazardous substances. Municipalities are responsible for school, care, traffic, street and park management, construction, etc. These responsibilities mean municipalities can influence other decision makers including residents and businesses through making informed choices, by making demands and by providing information. Criteria on hazardous substances must be integrated into public procurement practices (“green public procurement”). The NonHazCity partner municipalities are currently developing strategic Chemical Action Plans, and are approaching different institutions in their municipality to achieve a non-toxic everyday environment.

What enterprises can do

Enterprises, including SMEs, use a lot of products that contain hazardous substances in their operations. Hazardous substances could be in articles they produce, in services they perform and in the operation of their workshops, offices and sites. NonHazCity is implementing pilot actions with SMEs to promote the reduction of emissions of hazardous substances – for example at hair dressers and beauty salons, hotels and hospitals, cleaning services, dry cleaners and car washing facilities, carpenters and other small enterprises, print and copy shops, construction markets and many more. Targeted information material is produced and communication activities performed.

What inhabitants can do

We all use products containing hazardous substances in our daily life, in our household – detergents, body care, large varieties of plastics, textiles, paints, electronics; some we know, but many products we do not think of as containing “chemicals”. NonHazCity implements campaigns in its partner cities to make inhabitants more aware of their chemical use and help them to make informed choices leading to a reduction of emissions of hazardous substances from households.

Overall key messages

- The findings of the pilot screening and the source tracking studies showed that source control of hazardous substances can be a key measure for reducing chemical emissions into WWTPs, and into recipient surface waters such as the Baltic Sea.
- The control or restriction of hazardous substances in products, articles and materials used by the multitude of small scale emitters upstream of WWTPs is essential in order to protect aquatic life in surface waters and the Baltic Sea, as well as reduce the human exposure to hazardous substances.
- The frequent presence of hazardous substances in wastewater from residential areas should encourage municipalities to prepare information campaigns for residents and households about the hazardous substances in their daily life. Better information can cause the reduction of hazardous substances levels in one of the most difficult to control and dispersed source.

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ABBREVIATIONS AND GLOSSARY

Analgetic	class of pharmaceuticals that are used to stop pain
Biota	The living organisms in a given region
ECHA	European Chemicals Agency
EE2	17 α -ethinylestradiol, a synthetic estrogen
EU	European Union
CAS	Identifier assigned to a substance by the Chemical Abstracts Service (CAS)
Cd	Cadmium
CLP	EU regulation on classification, labelling and packaging
CMR	Substance with carcinogenic, mutagenic and reprotoxic properties
Cr	Chromium
DBP	Dibutyl phthalate
DEHP	Di(2-ethylhexyl)phthalate
DEP	Diethyl phthalate
DIBP	Diisobutyl phthalate
dm	dry matter
DMP	Dimethyl phthalate
DNOP	Di-n-octyl phthalate
ECHA	The European Chemicals Agency
HELCOM	Helsinki Commission, the body responsible for the implementation of the Helsinki Convention
HS	Hazardous substance/s
IA	Industrial area
MDL	Mean detection limit
mg/kg	Milligram per kilogram
μ g/L	Microgram per liter
NACE code	Statistical Classification of Economic Activities in the European Community
ng/L	Nanogram per liter
Ni	Nickel
NP	Nonylphenol
NPEs	Nonylphenol ethoxylates
OP	Octylphenol
OPEs	Octylphenol ethoxylates
Pb	Lead
PBT	Substance with persistent, bioaccumulative and toxic properties
PFAS	Perfluoralkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POP	Persistent organic pollutant
RA	Residential area
REACH	EU regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals
SME	Small and median enterprises
SS	Sewage sludge
SW	Stormwater
vPvB	Substance with very high persistence and very high bioaccumulative properties
WFD	Water Framework Directive
WWTP	Wastewater treatment plant
WWTP-ISW	Influent sewage water to WWTP
WWTP-ESW	Effluent sewage water from WWTP

ABOUT THE PROJECT

The project “Innovative Management Solutions for Minimizing emissions of hazardous substances from urban areas in the Baltic Sea Region” (NonHazCity) is financed by the European regional development fund within the Interreg Baltic Sea Region program, from March 2016 to February 2019. The project involves 18 partners from Sweden, Finland, Estonia, Latvia, Lithuania, Poland and Germany and 23 associated partners.

NonHazCity wants to demonstrate possibilities of municipalities and WWTPs to reduce emissions of priority hazardous substances (HS) from small scale emitters in urban areas that cannot be reached by traditional enforcement techniques. Substances of concern will be identified and prioritised, sources tracked and ranked, individual HS Source Maps and Chemicals Action Plans developed by each partner municipality.

Municipal entities will implement own substance reduction measures at their premises. Private small scale businesses will pilot substitution actions and improve their assortment. Inhabitants will be shown their HS emission share and test the use of less HS in every-days household management to help to protect the Baltic Sea environment but also their own health.

If you are interested to follow the project this newsletter will be produced about twice a year. It is also possible to read about activities at the project website www.nonhazcity.eu and at partner websites.



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