COHIBA

CONTROL OF HAZARDOUS SUBSTANCES IN THE BALTIC SEA REGION

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Substance flow analysis case study report of St.Petersburg city and Leningrad region (Russia)

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1 Contents

1 Introduction

Pollution caused by hazardous substances poses risks to the Baltic Sea area. Loads and impacts of some hazardous substances have been reduced considerably during the past 20-30 years, but concentrations of some other substances have increased in the marine environment. With HELCOM Baltic Sea Action Plan (BSAP) the Baltic Sea countries have committed themselves to achieve a "Baltic Sea with life undisturbed by hazardous substances". The overall objective of COHIBA is to support the implementation of the BSAP with regard to hazardous substances (**Table 1**) by developing joint actions to reach the goal.

Table 1: The 11 substances/substance groups identified in the Baltic Sea Action Plan to be of special concern.

1. Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs)
2. Tributyltin compounds (TBT), triphenyltin compounds (TPhT)
3. Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE)
4. Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA)
5. Hexabromocyclododecane (HBCDD)
6. Nonylphenols (NP), nonyphenol ethoxylates (NPE)
7. Octylphenols (OP), octylphenol ethoxylates (OPE)
8. Short-chain chlorinated paraffins (SCCP), medium-chain chlorinated paraffins (MCCP)
9. Endosulfan
10. Mercury
11. Cadmium

1.1 National summary

This report summarises the results of SFAs for each groups of priority substances in Russia from neiboring regions at the Baltic Sea – St.-Petersburg and Leningrad Region. These results will be used in COHIBA project to make a joint assessment of the most important sources of hazardous substances in the Baltic Sea region.

2 Sources and flows of the target substances

During this work firstly identification of sources and evaluation of possible loads of Baltic See Action Plan (BSAP) substances in the environment in Russia (St.-Petersburg and Leningrad Region) was realized. These substances are not produced in mentioned regions of Russia but used in manufacture and private consumption of various goods and chemical products. As unintentional side-products of high temperature burning processes in manufacture, energy production and accidental fires dioxins/furans are formed.

Total yearly load of target substances (without dioxins) by mass is estimated in range of **157,9 – 197,7 tonnes**. Emission of dioxins attains about **44,5 g I-TQE/year**. The most important domains emitting target substances in the environment are: Private consumption during lifetime use of articles, goods and chemical products/preparations (about 49 % by total mass of yearly emitted substances), Activities outside St.-Petersburg city and the Leningrad Region (long-range transboundary air pollution, about 18 %), Sewerage (effluents and waste water treatment sludge, about 3%) and Waste management sector (about 0.8%). Emissions of target substances from manufacture is not relevant in this report because there were poor information and data from this sector in Russia. The most important pollutants from target substances are Cadmium, OPE, NPE, NP, SCCPs, PBDEs and Mercury putting together almost 100% (99,4%) by mass from yearly load of BSAP substances in St.-Petersburg and Leningrad Region. Total yearly load of hexabromocyclododecane, perfluorooctanesulfonates/perfluorooctanesulfonic acid, tributyltins/triphenyltin, octylphenols and endosulfan (all together) could be evaluated as unsubstantial for target regions (<0.6% from summary load of target substances) .

Due to the lack of reliable data and infromation concerning target substances in Russia the most part of estimations was made by scaling with EU data with big uncertainties (C). More or less bookworm information was found about mercury emissions.

2.1 Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs)

In the Soviet Union until 1970, about 60% of PCBs used in closed systems of heat and electric power transfer, 25% as a plasticizer, particularly in the manufacture of carbon paper, and less than 5% in the manufacture of pesticides. Currently, legal use is banned, but still a large number of these compounds are used in large condensers and transformers. In Russia, PCBs were produced by several companies, but not in St. Petersburg and Leningrad region. After 1990-93 these enterprises are completely stopped production of PCBs, no stocks of PCBs remain. Possible occurrence place of PCBs in Russia is electrical equipment (condensers, transformers) in the fuel and energy sector, ferrous and nonferrous metallurgy, chemical, petrochemical and forestry sectors, engineering and other industries. According to expert estimates in St.Petersburg, 33 enterprises have transformers and condensers containing PCBs. Total number of transformers - 94, condensers - 6393. Amount of PCBs contained therein - 975 tons. St.-Petersburg’s experts estimate a risk of contamination from PCB’s companies in the region is 0.5 - 3.0 company/km^2.
In general according to experts at the present time in Russia dioxin and furan emissions to air are 650-800 g TEQ/year. Main industrial enterprises given environmental pollution by

dioxins are located in the Central, Ural and North-West economic regions of Russia. The largest sources of pollution are following sectors:

- manufacture of building materials;
- manufacture of wood, pulp and paper;
- chemical and petrochemical industry;
- iron and steel production;
- non-ferrous metal production;
- electric power industry.

Relevant sources of dioxins and furans in the environment are also environmentally unsafe technologies for destruction, disposal and recycling of hazardous waste, including incinerators.

Monitoring of environmental pollution in Russia is carried out by Federal Hydro Metrological and Monitoring Service (RosHydroMet). The most toxic POPs (PCDDs and PCDFs) are not controlled by RosHydroMet due to their determination requires chromatography-mass spectrometry analysis, but this complicated test method of dioxins, furans, biphenyls, toxaphene (polychloropinene and polychlorocamphene) used only by specialized laboratories. Implementation of this analytic method of POPs testing (particularly dioxins and furans) into RosHydroMet network is still too expensive. Monitoring of dioxins and furans is part of some international and regional programs.

Wastewater treatment facilities are one of the biggest sources of POPs emissions because they treated considerable waste water (and surface running and rain water) amount and accumulate POPs in wastewater treatment facilities sludge. In 2008 within quality effluents studies in WWTPs of St-Petersburg dioxins and furans were not found, the concentrations of dioxin-like PCBs were in range 0.05632 – 0.16751 pg/l. There were not studies of sludge.

In November 2009 within BaltHazar project few studies of leachate samples from four landfills in St.-Petersburg and Leningrad Region and sediment of the Izhora River were made. Concentration of PCBs (sum of 14 congeners) was in range 0,14 – 123 ng/l, concentration of PCDD/PCDF 0,321 – 19,8 ng/l I-TEQ. There are 28 legal landfills of PCBs in St.-Petersburg and Leningrad Region, but investigations of them are not conducted. Soil contamination by PCBs in 2008 in St.-Petersburg was 0,03 – 1,2 mg/kg.

According to the most recent data in this report, the major sources of dioxins to the air in St.-Petersburg and Leningrad Region of Russia were wastewater treatment sludge incineration (56%), heat and power production (26%), secondary aluminium products manufacture (10%) and iron and steel production (7%). Also secondary aluminium products manufacture is most significant source of dioxins to waste – 18,4 g I-TEQ. Most significant and single source of PCBs to the surface water is effluent from WWTPs.

According to the recent official data, dioxin emissions in Russia tend to decrease. In future further scanty decrease of air emissions can be expected with BAT improvements in iron and steel production, power production and waste management. Climate conditions can influence this significantly.

2.2 Tributyltin compounds (TBT), triphenyltin compounds (TPhT)

TBT and TphT compounds were used as far back as in Soviet Union as a stabilizer of polyvinyl chloride (PVC), as fungicides (tributyltin oxide, tributyltin methacrylate), bactericides (tributyltin benzoate), biocides in antifouling paints for ships. Currently the using of organotin compounds as fungicides in Russian Federation is banned. The 1992 Helsinki Convention bans the application of antifouling paints containing organotin compounds on pleasure craft less than 25 m in length and on fish net cages. Also the use of TBT in antifouling paints has been banned by the 2001 International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention), which entered into force in 2008. Russia has not still ratified the Convention however TBTs in antifouling paints are not use in St.-Petersburg (SPB) and Leningrad region (LO) by HELCOM requirements and local legislation on regional level. Furthermore tri-organotins are included into the list of hazardous substances prohibited to discharge in exclusive economic area of Russian Federation from ships, aircrafts, man-made islands, plants and facilities. There are not any available and measurement data concerning the application tri-organotins in any industry and particularly in PVC production. In addition by studies of effluent quality from WWTPs of St.-Petersburg within pilot investigations in 2008 the TBT and TPhT compounds were not found. Also tri-organotins were not detected in the leachates from some landfills of St.-Petersburg and Leningrad region and sediments in 2009 within BaltHazar project.

There are no consistent monitoring data on emissions of organotin compounds in Russia and information regarding emissions of tributyltin and triphenyltin compounds in environment is very scanty. Since production of iron and steel as well as cement exists in St.-Petersburg and Leningrad region, possible emissions with waste water to WWTPs was estimated in the frame of COHIBA project. Due to the lack of data on landfill areas and leachate volumes quantitative estimation of organotin emissions from landfills was not possible. Also according to the results of BaltHazar project there are not tri-organotins in leachate from landfills and sediments. Another source of organotin contamination could be sediments harbours and coastal waters but at present there are not sufficient convincing measurement data to assess this kind of pollution properly. There are no emission data for estimation of total organotins in air.

As available information about production of products containing TBT is indicative that tributyltin and triphenyltin compounds are not used in production processes, it can be assumed that this type of manufacture will not develop in Russia particularly in St.-Petersburg and Leningrad region as boundary subjects of Russian Federation legally obligated the international requirements.
Taking into account that navigation in Russian coastal waters is fairly intensive, TBT leaking from this activity will continue for some more years ahead.

2.3 Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE)

PBDEs neither as substances, nor as articles or goods containing PBDEs were produced in Russia and appropriately in St.-Petersburg (SPB) and Leningrad Region (LO). However PBDEs are found in waste water from municipal waste water treatment plants (WWTPs) of St.-Petersburg. Still substantial stocks may be stored in products in use in the society. These substances could be placed mainly in such imported commodities as clothing, upholstered furniture, computers and TV sets.

2008 pilot investigation of effluents quality at three biggest WWTPs in St.-Petersburg has been done. Concentration of penta-, octa- and deca BDEs in waste water discharging to water basin was average <0.1 μg/dm^3.
In November 2009 within the BALTHAZAR project ("Protection of the Baltic Sea from pollution through reducing of loading caused by agricultural entities and hazardous wastes) also one complex sample of sediments in the Izhora River (Leningrad Region) has been done. Concentration of PBDE in water has the wide range <1 – 24.8 ng/dm^3. Also six landfills were studied in the Leningrad region: landfill 'Ust-Tosna', dumping area "Primorskaya", MSW landfill "Novoselki", MSW landfill "Volkhonka", Industrial waste landfill in Gatchina town, MSW landfill in Gatchina town. Concentration of PBDE in water of drainage ditches around landfills has the wide range <7 – 100 pg/dm^3.

2007 – 2008 Chemical-Analytical Centre "Taifun" has made the studies of outdoor air pollution of PBDEs in some cities of Russian Federation including Moscow (approx. 765 km far from SPB) and Arkhangelsk (1181 km far from SPB, North-West of Russia). Average concentrations of BDEs in outdoor air were: in Moscow – 0,06 – 1,88 pg/m^3; in Arkhangelsk – 0,06 – 0,54 pg/m^3 (congeners 47, 99, 100, 183, 209). (Report on condition and pollution of environment in Russian Federation in 2008. Russian Federal Service for Hydrometeorology and Environmental Monitoring (RosHydroMet).

The main sources of PBDEs presence in environment of SPB and LO regions of Russia are transboundary air pollution and effluent from WWTPs. Figures are associated with major uncertainties. Atmospheric deposition is estimated to be the absolute dominant pathway to the remaining media.

By estimation loads of PBDEs in waste water Vodokanal St.-Petersburg measurement data on PBDE concentration in effluent were used. By estimation percentage distribution in compartments (agricultural land, forest land, inland surface waters) the data of St.-Petersburg and Leningrad Region Government were applied, which differ from the average EU data. In other cases when statistical data and national emission factor are missing the load was estimated based on EU example.

PentaBDE
The most important sources to **outdoor air** for pentaBDE appear to be activities outside SPB/LO regions (99/99.9%), followed in SPB by emissions from steel production (0.3%), in LO by emissions from private consumption of articles and goods. For **indoor air**, emissions from private consumption of articles and goods are the one source. For **surface water** sewage (99.9%) is the main source of pollution. For **agricultural soil** (practically 100%) and for **forest soil** atmospheric deposition (100 %) is the main source of pollution.

DecaBDE
The most important sources to **outdoor air** for decaBDE appear to be transboundary air pollution (99%). Amount of emissions for **indoor air** from electrical appliances was not been done due to lack of data. For **surface water** (100%) sewage is the main source of pollution. **For agricultural soils** (particularly 100%) as well as for **forest soils** (100%) atmospheric deposition is the most important.

Emissions and loads of PBDEs in St.-Petersburg and Leningrad regions environment are not quite big. Since 2010 import of PBDEs as substance and as articles, goods and waste containing PBDEs is banned, also PBDEs are not produced and used in these regions. Therefore it is anticipated that emissions will be reduced likewise further, but the influence of an extensive diffuse leakage from articles in use on the global scale and transboundary air pollution will survive.

2.4 Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA)

PFOA can be used in polyperfluoroethylene (PPFE) manufacturing. Two big producers of PPFE are known in Russia. In St.-Petersburg two small-scale enterprises manufacture the products containing PPFE. Total volume of fluorpolymers production in Russia could be estimated approx. 100 000 tonnes per year (<0.1% of world manufacturing) according to www.polymery.ru.

Unfortunately there is not reliable available information about using of PFOS or PFOA or its derivatives during abovementioned processes in Russia. Presumably PFOA and its derivatives can be used all the same in fluoropolymers production.

There are not monitoring data of PFOS and PFOA concentrations in the environment. However PFOA has been found in the samples of effluent at three big WWTPs of St.-Petersburg within pilot studies in 2008. Rough estimation of PFOA's concentration was <0,1µg/l.

PFOS, PFOA and its derivatives are not regulated and monitored in the environment in Russia and not legally controlled in the industrial manufactures. These substances could be used in eg. polyperfluoroethylene manufacturing, in metal (chromium) plating, manufacture of semi-conductors in St.-Petersburg city and Leningrad Region but due to the lack of information it is difficult to estimate the emissions from these potential sources. Estimations were made for PFOS/ PFOA emissions from municipal STPs, consumer lifetime use of articles, goods and chemical products, waste management as well as emissions in air for PFOA (as impurity in PFOS based products and due to degradation of fluorotelomer raw materials).

PFOS
The most important source to the environment for PFOS appear to be consumer lifetime use of articles, goods and chemical products: 85 kg to waste water, 92 kg to outdoor air, 0,8 kg to the land (St.-Petersburg) and 29,4 kg to waste water, 32 kg to outdoor air, 0,3 kg to the land (Leningrad Region). Second main source appear to be WWTPs: 33 kg to surface water and 19,9 kg (worst case) to the land (St.-Petersburg) and 12 kg to waste water and 8,1 kg (worst case) to the land (Leningrad Region). As the PFOS emissions often were estimated by using

analogies with EU estimates, uncertainty of these estimations is high and the made estimates could be overestimated for these regions of Russia.

PFOA

Estimated PFOA emissions are in general lower than PFOS emissions. The major emission sources for PFOA are municipal and some industrial STPs and secondary sources such as release of PFOA due to degradation and the presence as impurity in articles. Emission estimates are however very rough and should be interpreted with caution.

Existing in force legislation has already decreased use and emissions of these substances. But as PFOS/PFOA substances are persistent and are tended to accumulate in environment emissions will decrease gradually.

2.5 Hexabromocyclododecane (HBCDD)

Currently in Russia HCBDD is produced (but not in St.-Petersburg and Leningrad Region), imported (mainly from China) and used as fire-retardant agent for the production of polypropylene, foam plastics, as well as a flame retardant for gums.

In Russia HBCDD is produced at least by one enterprise in Altaian Krai. On the market of St.-Petersburg and Leningrad Region are there at least two big company-distributors of chemicals which provide also HCBDD from Chinese and European producers. The store of chemicals allocated in Leningrad Region (Yanino). Code of Stock List of Foreign-Economic Activity (TN VED) 2903598000. Hexabromcyclododecane (HBCDD) (ГБЦД) FR-1206- Flame retardant to protect foam polystyrene from fire.

HBCDD is used generally as a flame retardant, mainly within the polymer and textile industry. This substance could be used also in production of latex adhesive, unsaturated polyesters and various surfaces. Last time HBCDD is substituted actively by halogen-free organics due to the high toxicity of HCBDD by their decomposition at high temperatures.

HCBDD was detected in single sample of the effluent at St.-Petersburg's WWTPs - <0,1 µg/l, and also in the leachate from (<50 pg/l) and sediments (<10,0 ng/kg).

Due to the lack of statistic data it was impossible to estimate the emissions from the industries and using of articles and goods. Approximate estimation of emissions from WWTPs, landfills and atmospheric deposition has been made. Most probable the load of HBCDD to the environment could be higher because the emissions from the industry were not included.

The main sources of emission of HBCDD in St.-Petersburg and Leningrad Region are:
for St.-Petersburg city:

- Sewerage (emissions of HBCDD with municipal STPs effluents) – estimated yearly load to surface waters - 33 kg;
- HBCDD accumulated in sewage sludge – estimated yearly load to the land (from the landfills) – 0,27 kg;
- Worldwide activities outside St.-Petersburg, for example atmospheric deposition of long range transport (estimated emissions: 0.01-6.8 kg/year on region, from which 0.01–0.68 kg/year of HBCDD are deposited on inland surface waters).

for the Leningrad Region:

- Worldwide activities outside Leningrad Region, for example atmospheric deposition of long range transport (estimated emissions: 0.61 – 398 kg/year on the region, from which - 0.12 – 79.6 kg/year to land used for agriculture and 0.34 – 218.9 kg/year to forests. About 0.15 – 97.5 kg/year of HBCDD are deposited on inland surface waters).
- Sewerage (emissions of HBCDD with municipal STPs effluents) – estimated yearly load to surface waters - 12 kg;
- HBCDD accumulated in sewage sludge – estimated yearly load to the land (from the landfills) – 9,6 kg.

Last time HBCDD is substituted actively by halogen-free organics due to the high toxicity of HCBDD by their decomposition at high temperatures. Therefore assumed, emissions of HBCDD might decrease in Russia, compared to the present estimates, in the future

2.6 Nonylphenols (NP), nonyphenol ethoxylates (NPE)

Nonylphenol (NP) is not produced in St.-Petersburg and the Leningrad Region but imported from EU countries (basically from Germany) and China. According to data base of Foreign Economic Activity Code Nomenclature (FEACN) and Russian Register of Potentially Hazardous Chemical and Biological Substances (RRPHCBS) (http://rpohv.ru) nonylphenols are used in chemical industry, metal processing, and rubber production also in mixtures as catalyst for polymer production.

Nonylphenol ethoxylates are produced by some Russian chemical enterprises but not in target regions (St.-Petersburg and Leningrad Region) considering in this report furthermore most part of NPEOs on the Russian market are imported from China, Taiwan and Finland. Nonylphenol ethoxilate (trade names Neonol AF 9-4, 9-10,12; Kemira M-246) can use in chemical, textile, pulp-and-paper industry, as component in detergents, in paints and as flotation reagent.

The primary source of nonylphenols found in the environment in St.-Petersburg and Leningrad Region is considered to be nonylphenol etoxylates, which can break down into NP in wastewater treatment plants or in the environment. Also products containing nonylphenol and nonylphenol ethoxylates are potential sources of diffuse emissions of nonylphenol and nonylphenol ethoxylates. If nonylphenols reach the marine environment this is generally via industrial or municipal wastewater.

Nonylphenols and nonylphenol ethoxylates are detected in single sample of effluent water from WWTPs in St.-Petersburg in average concentration $<0,1$ μg/l.

In St.-Petersburg and Leningrad Region nonylphenols can be used in chemical industry, metal processing, and rubber and rubber articles manufacture also as component in various mixtures for polymer manufacture. However, due to the lack of any information and data on amount of used NPs it was impossible to estimate emissions from these sources. All other estimations have been done by extrapolation of EU data given in *SFA Nonylphenol (EU27)*. From these study emissions from private consumption during lifetime use of articles, goods and chemical products, id etc, washing of textiles and use of cosmetics and hygiene products is shown to be the most important source of emissions of nonylphenols. Yearly emission to wastewater from use of cosmetics and hygiene products and household washing of textiles are estimated in range of 1.2-356.3 kg and 6,8 tonnes, respectively, for St.-Petersburg and 0.4-127.3 kg and 2.4 tonnes, respectively, for Leningrad Region.

Another source of nonylphenol emissions in environment is lanfilled sewage sludge to the land: 35.4-91.2 kg/year for St.-Petersburg and 1261-3249.7 kg/year for Leningrad Region. Emissions of NPs with effluent water from municipal STPs have been calculated with high uncertainty so long as used emission factor is not quite representative. Yearly atmospheric depositions to the land area are estimated is not very big therefore this source is not relevant.

The major source of NPEO to the environment in St.-Petersburg and Leningrad Region is the washing of textiles in household – 31 tonnes/year (could be overestimated). Second largest source of NPEO in Leningrad Region is the disposing of sewage sludge on the landfills – in range 167,1 – 371,2 kg/year (also could be overestimated).

According Russian classification of hazard for chemical substances NPs and NPEO belong to moderately hazardous substances and not still banned for use and import. Therefore the big reduction of NP and NPEO emissions is not expected next years.

2.7 Octylphenols (OP), octylphenol ethoxylates (OPE)

Octylphenols (OPs) are produced in Russia but not in St.-Petersburg city and the Leningrad Region but probably could be used as components in production of chemical mixtures or preparations but there are no any reliable data regarding their application. Most part of octylphenols (generally 4-tert-octylphenol) on the market of these regions is imported from China, India, Iran and UK. Octylphenols could be applied as stabilizer in various industrial braches (e.g. manufacturing of rubber articles, pulp production). At least one producer of OPs in Russian is known. This petrochemical plant in the Central Region of Russia manufactures 1700 tonnes of octylphenol (trade name Neonol AF14) yearly (*www.tatcenter.ru*).

OPEs are also not produced in St.-Petersburg and Leningrad Region of Russia. OPEs are imported from China, India and UK. OPEs could be used in some economic sectors; however there is no reliable information about their application in the target regions of Russia. According to data base of Foreign Economic Activity Code Nomenclature (FEACN) diethylene glycol octylphenol ether (code 2909440000) is used as component of cosmetic preparations (www.tamognia.ru).

Octylphenols are detected in single sample of effluent water from WWTPs in St.-Petersburg in average concentration <0,1 μg/l.

Due to the very poor information it was difficult to get convincing quantitative magnitudes regarding emissions of octylphenols in environment in St.-Petersburg and Leningrad Region of Russia. Quantitative estimation was made on amounts of OPs emissions to the surface water (in range 3,2 – 109,5 kg/year) and to the soil (in range 64,7 – 207,9 kg/year) only from WWTPs. Washing of textiles could be important source, but output data for estimation are insufficient (volumes of wastewater from laundries, average concentration of OPs is not known).

Washing of imported textiles is shown to be important, and possibly the most important sources of emissions of octylphenol etoxylates in St.-Petersburg and Leningrad Region of

Russia, with a yearly emission of 39.3 tonnes to waste water. However, the estimates in this calculation are rough, with a high uncertainty and could be overestimated, because of use of imported textiles in Russia could be under the EU average (17 kg/person) value.

Due to the lack it was impossible to estimate emissions from all potential sources of Ops and OPEs in St.-Petersburg and Leningrad Region.

According Russian classification of hazard for chemical substances OPE belongs to low hazardous substances and not still banned for use and import. Therefore big reduction of OPE emissions is not expected next years.

2.8 Short-chain chlorinated paraffins (SCCP), medium-chain chlorinated paraffins (MCCP)

Short-chain chlorinated paraffins (SCCPs) are not produced in St.-Petersburg city (SPB) and Leningrad Region (LO) and according to *SFA Chloralkanes C10-C13 (EU27), draft ver,1.2, 28.06.2010* SCCPs are not produced in Russia on the whole. Short-chain chlorinated paraffins could be used by manufacture of leather, fabricated metal products, and rubber and plastic products, as well as in textile industry and as additive to paints. Since 2000 SCCPs were banned for discharge from ships, aircrafts, man-made islands, plants and facilities in exclusive economic area of Russia.

Chlorinated paraffins C14-30 are produced in Russia on industrial scale but not in St.-Petersburg city and Leningrad Region. MCCPs can be used by metal processing under a pressure; as additives; as plasticiser in paints; leather processing; as fat emulsion, also applied in manufacture of PVC and carbonless copy paper.

There are no measurements of MCCPs in environment in Russia. MCCPs were found in effluent samples from 3 WWTPs of St.-Petersburg in concentration approx. <0,1 µg/l (samples from 2008)

The one of the most important source of SCCPs emissions in Leningrad Region is sewage sludge from municipal STPs, giving a yearly total load of 342 - 1219 kg of SCCPs to the land; in St.-Petersburg most amount of sludge is incinerated therefore emissions are not big - 9.6 - 34.2 kg of SCCPs to the land and this source is not relevant for the city..
The second largest source of emissions is private consumption (use of products), giving a yearly load of 560 - 1560 kg of SCCPs in environment (34 - 128 kg/year to air; and 527 – 1440 kg/year to wastewater). However for this sources the volatile and leaching losses over lifetime from rubber and plastic products containing SCCPs and from surfaces painted with SCCP containing paint were left out of account due to the lack of data.
The next largest source of emissions is the waste remaining in environment. Yearly load to soil is estimated about 0.4-0.79 tonnes for SPB and 0,14-0.28 tonnes for Leningrad Region.

The estimated emissions of SCCPs are mainly based on EU data from 2001 and calculated according to the methodology given in *Report SFA Chloroalkanes C10-C13 (EU27) Draft vers.1.2.*
As the one of main sources of emissions are sources with sometimes long service-life, there will be a delay in the effect of reduced use and decrease of the yearly releases to the environment.

Due to the lack of data the full load from potential sources of MCCPs were not estimated. The calculation of emissions from STPs to surface water has been done only. Emissions in St.-Petersburg were estimated as 33 kg per year, in Leningrad Region – 12 kg per year.

The MCCPs have rather similar uses as the short-chain (C_{10-13}) chlorinated paraffins and can be considered as replacements for the short-chain chlorinated paraffins in some of applications. This could lead to an increased use of MCCPs as a replacement.

2.9 Endosulfan

Use of endosulfan was restricted yet in 1982 in Soviet Union. According to *Annual State catalogue of pesticides and agrochemicals allowed for the use in Russian Federation* use of endosulfan as a plant protection product was banned from the 1990 years.

No one of endosulfan forms was produced in Russia. This concerns the mixtures of endosulfan with other chemical substances also. Endosulfan or its formulations were never legally used in Russian Federation.

Endosulfan has been detected in few samples of leachate from four landfills in the Leningrad Region within BALTAZAR project in range 0 – 1,11 ng/l and in one sample of sediment in the Izhora river with concentration 0,25 mg/kg.

There are two main sources of endosulfan in St.-Petersburg and Leningrad Region in environment: long-range transboundary air transfer (0,43 – 57,9 kg/year to soil and 0,18 – 24,9 kg/year to surface water) and WWTP (3,66 kg'year to surface water), input from consumption of imported foodstuffs is minor.

The estimations are however associated with large uncertainties and the data presented should be interpreted with caution.

2.10 Mercury

Total mercury consumption in Russian Federation over the past 20 years has decreased significantly (in 2.5 - 3 times). Production of primary mercury ceased in 1995, currently most of mercury used in the chemical industry (production of chlorine and caustic soda, vinyl chloride), in manufacture of mercury thermometers and fluorescent lamps. Application of mercury for production of electrical appliances and measuring equipment also decreased markedly in recent decades. In St. Petersburg and the Leningrad region single manufacturer of caustic soda was closed in 1993, also in these regions are not produced measuring devices containing mercury, mercury-vapor lamps, mercury and mercury-containing chemicals and pesticides.

Mercury consumption for manufacture of dental amalgam fillings reduced in several tens of times (from 6 tons in 1991 to 0.8 tons in 2001) and this trend continued into the present (*Assessment of Mercury Releases from the Russian Federation, Report ACAP, 2005*).

Use of mercury for gold mining using amalgamation method was banned in Russia over 20 years ago. Also, there is currently no commercial production of mercury-containing pesticides and biocides and their use is prohibited.

Main source of mercury emissions in Russia could be refining and use of petroleum products, coal combustion and other fossil fuels, as well as plants in primary smelting of nonferrous metals.

Since 2010 import of wastes, whose composition as a component or contaminant comprises mercury, mercury compounds, slag, ash and residues containing mercury, used mercury lamps and fluorescent tubes to Russian Federation is banned (*List of hazardous waste and products prohibited to import in Customs Union. Resolution N132 of Customs Union Commission EvrAzEC from 27.11.09 "On united nontariff regulation of Customs Union of Belarus, Kazakhstan and Russian Federation").*

At present in St. Petersburg has been in operation about 18 - 20 million fluorescent lamps of various types. The most common types of fluorescent and special mercury lamps contain from 20 to 300 mg of mercury. Each year, goes down about 8 - 9 million lamps. Collection, defusing, transportation and disposal mercury and mercury containing devices carried out by companies having permission for this activity. Recycled mercury wastes are disposed in special landfills. In 2009 municipal environmental emergency service to eliminate chemical and radiological contaminants has been collected 128.4 kg of mercury, 20 043 medical and 683 technical mercury thermometer, mercury-containing devices 88, handled 500 thousand luminescent lamps (*Report of the Committee for Nature Use, Environmental Environment and Ecological Safety of St. Petersburg's Government, 2010).*

Heavy metals, including mercury and cadmium, are priority substances and their content is monitored in the environment. According to data of quality monitoring of effluents discharged from sewage treatment plants in St. Petersburg, the concentration of mercury in waste water in 2009 did not exceed setting regional standard (<0.00001 mg/l). According to the Committee for Nature Use, Environmental Environment and Ecological Safety of St. Petersburg's Government the concentration of mercury in surface waters of St. Petersburg in 2009 did not exceed the setting MPC (0.0005 mg/l). According to the Federal Hydro Metrological and Monitoring Service (RosHydroMet) in 2008 the mercury content in the soil in St. Petersburg was 0.03 - 2.1 mg/kg, ie at the limits of the MPC. Disposal of hazardous waste on the territory of St. Petersburg and Leningrad region carries only one company GUP Landfill "Krasny Bor". Since the entry into force in early 1970 at the site has collected about 1.7 million m^3 of hazardous waste of different hazard classes in the area of 50 hectares. It is known that at the site contains at least 100 tons of mercury (*ACAP, 2005).*

Significant source of Hg emissions in air is mining activities (mining of oil shares) – about 500 kg/year and waste management sector (incineration of industrial and clinical hazardous waste) – about 232 kg/year. Cement production also emits relatively big amount of mercury in air – 90 kg/year.

Important source of mercury emissions in water is sector Activities of household (Emissions in human excrements) – about 38,5 kg/year with waste water. Waste water treatment plants are responsible for 21 kg of the mercury emissions to surface water.

Atmospheric deposition to land seems to be very important - 2.1 tonnes/year.

Total mercury consumption in Russian Federation has decreased over the past 20 years, respectively, reduced emissions of mercury to the environment. In the coming years these trends will continue.

2.11 Cadmium

There is no stock of metal containing ores, including cadmium, in St.-Petersburg and Leningrad Region. Therefore fossil fuel combustion plants, ferrous and nonferrous metallurgy, as well as atmospheric depositions seems to be the major anthropogenic sources of cadmium emissions in the environment.

Cadmium metal
Neither cadmium, nor cadmium compounds is not produced in St.-Petersburg and Leningrad Region. There is no production of cadmium from zinc sulphide ores or other non-ferrous metals such as lead in these regions. Therefore cadmium can be not obtained as a by-product in the refining of these ores. Production of cadmium as a secondary product through recovery from Ni-Cd batteries in recycling plants is also not in place.
Cadmium oxide and other compounds
The substance is important commercially for itself and also because of its extensive use in the preparation of other cadmium compounds. As mentioned before, cadmium oxide is not produced in St.-Petersburg and Leningrad region.

Cadmium metal exhibits excellent technical qualities - resistance to corrosion, particularly in alkaline and seawater environments, rapid electrical exchange activity and high electrical and thermal conductivity. Cadmium pigments produce intense yellow, orange and red colours, and are widely used in plastics, glasses, ceramics, enamels and artists' colours. Cadmium metal and cadmium compounds are used as pigments, stabilizers, laboratory chemicals, conductive agents, in coatings, in rechargeable nickel-cadmium batteries.

According to the Federal Hydro Metrological and Monitoring Service (RosHydroMet) in 2008 the cadmium content in the soil in St. Petersburg was in range 0.17 - 10.5 mg/kg, i.e exceeded the limits of the MPC. In 2008 concentration of cadmium in effluents from WWTPs of St.-Petersburg was in range 0,00011 – 0,00023 mg/l. In 2009 according to data of the Committee of Nature Use, Environment Protection and Ecological Safety the cadmium and cadmium compound are not found in effluents discharging to water basins of St.-Petersburg. In 2009 cadmium was found in three samples of leachate from four landfills in Leningrad Region within BaltHazar project (*SFA PBDEs, Russia, ver.2, May, 2011)* with concentration in range 0,00008 – 0,0017 mg/l and in one sample of sediment in the Izhora river with concentration 2,3 mg/kg.

In compare with mercury there is poor data about emissions of cadmium in Russia and especially in St.-Petersburg and Leningrad Region. Therefore it was impossible to estimate emissions of Cd from potential industrial sources. Combustion of fossil fuels and energy sector could be important sources of Cd emissions in air but due to the lack of data the load was not estimated. According to this SFA the major Cd emission sources to water are emission from private consumption: release when washing & cleaning with detergents – 16.7 kg; emissions from use of fertilizers in private and market gardening – 5 kg; release during use of artist paint – 32.2 kg; emissions from tapwater – 4.1 kg; emissions from consumption of food – 24.8 kg. Significant source of Cd emissions in water were also construction – 0,08 – 80,6 kg/year.

Emissions to surface water are dominated by atmospheric deposition 27 tonnes/year and seem to be overestimated. However measurement data to evaluate this magnitude correctly are missing.

For emissions to soil atmospheric deposition is dominating – about 2.1 tonnes. The use of phosphate fertilizers and car washing could be important sources but due to the lack of data the estimation of the load was not done.

The use of fertilizers and the contamination of Cd in the used phosphates is a problematic issue. As long as expensive technical treatment is not used during the production of fertilizers, this will be even more problematic in the future. When it comes to point sources, like energy and metal production better treatment should be managed. Decreasing emissions to air (worldwide) would be an important measure as atmospheric deposition is an important source of Cd.

2 Summary and conclusions

2.1 Emissions to the environment

The preliminary results regarding emissions and yearly loads of target substances are reflected in **Table 2**. Total estimated yearly loads in environment are in range 35,6 – 42,4 tonnes. The highest emission of target substances is on surface water (FSW, about 84% from totals). Table does not reflect full picture, because of scanty monitoring data in Russia and especially in St.-Petersburg and Leningrad Region as well as there is no sufficient statistic data on industry. It was difficult to divide emissions to inland surface water (FSW) and to coastal surface water (CSW) due to the lack reliable statistic information on the marine squre in target regions and available methodology for that.

Table 2: Summary of emissions to environmental matrices. (kg/year)

Substance/ substance group	Total emissions to:				
	FSW	CSW	FS	AS	AO
1. Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs)	0.076-0.2367 g I-TEQ	NE	NE	NE	25.9 g I-TEQ
2a. Tributyltin compounds (TBT),	NE	NE	NE	NE	NE
2b. Triphenyltin compounds (TPhT)	NE	NE	NE	NE	NE
3a. Pentabromodiphenyl ether (pentaBDE)	142.6-280.8	NE	2.8-316	1.1-93.5	0.197-0.75
3b. Octabromodiphenyl ether (octaBDE)	This substance group has not been assessed separately.				
3c. Decabromodiphenyl ether (decaBDE)	142.6-614.6	NE	2.2-985.6	0.8-297.5	0.23-1.9
4a. Perfluorooctane sulfonate (PFOS)	45.3	NE	5.1	NE	0.12-0.24
4b. Perfluorooctanoic acid (PFOA)	45.0	NE	0.088	NE	0.69-15.42
5. Hexabromocyclododecane (HBCDD)	45.2-153.8	NE	10.3-228.8	0.01-79.6	NE
6a. Nonylphenols (NP),	46.5	NE	1296.4-3341.2	NE	NE
6b. Nonyphenol ethoxylates (NPE)	46.5	NE	167.1-380.2	NE	NE
7a. Octylphenols (OP)	3.2-109.5	NE	64.7-207.9	NE	NE
7b. Octylphenol ethoxylates (OPE)	91.3	n.d. **	39.6-50.6	NE	NE
8a. Short-chain chlorinated paraffins (SCCP)	45.7-79.4	NE	887.6-2317.2	NE	222-525
8b. Medium-chain chlorinated paraffins (MCCP)	45	n.d.	NE	NE	NE

Substance/ substance group	Total emissions to:				
	FSW	CSW	FS	AS	AO
9. Endosulfan	2.8	NE	NE	NE	NE
10. Mercury	2121	NE	100	NE	822.3
11. Cadmium	27005-27091	NE	2100	NE	NE
	29827.7 - 30491.7		4675.9 - 10032.7	1.91-470.6	1046.5-1365.6

FSW: Fresh surface water (inland surface water)
CSW: Coastal surface waterx z
AS: Agricultural soil
FS: Forest soil
AO: Air outdoor

***NE**- not estimated
** n.d. – not detected

2.2 Indoor air

In the frame of COHIBA project as main pollutants in indor air pentaBDE, decaBDE and PFOA are identified.Private consumption during lifetime use of articles, goods and chemical products, as well as use of electric&electronical appliances in service sector is the source of these emissions. Estimated by extrapolation from EU data to the Russian conditions amount of pentaBDE to indoor air was 69.8 kg (for 2007). Yearly emissions of pentaBDE from use of TV sets and personal computers (PC) were not estimated due to the lack of statistical data about an amount of TV sets and PC in target regions in 1997-2005. Therefore the load to the environment is underestimated. DecaBDE was estimated in smaler amount – 0.012- 0.48 kg. PFOA is estimated in range of 0.244-13.036 kg due to degradation processes of fluorotelomer raw materiāls in ready made products.

2.3 Transfer to waste and sewerage

Private consumption of articles and goods to sewerage is one of the most significant sources of emissions in St.-Petersburg and Leningrad Region (94.3-127.2 tonnes) basically by NPs, OPEs and NPEs. Taking into account that almost calculations were made by scaling with EU data these figures could be overestimated.

Waste management sector could be one of the largest sources of emissions. Most part of sewage sludge in St.-Petersburg (99%) is incinerated therefore this sector is relevant source of dioxins emissions. Information regarding wastes going to landfill disposal is poor and is limited with data on amounts. Regular monitoring data from waste polygons including information on landfill areas, volumes and composition of leachates are in the very beginning and incomplete. Number and capacity of waste treatment plants is low and information from waste treatment and processing scanty.

Still data and information is lacking on volumes and composition of waste waters from such sources as car washing, loundries.

2.4 Conclusions

According to preliminary results from SFAs made by COHIBA methodology in St.-Petersburg city and the Leningrad Region the most important domains emitting target substances in environment are: Private consumption during lifetime use of articles, goods and chemical products/preparations (about 49% by total mass of yearly emitted substances), Activities outside St.-Petersburg city and the Leningrad Region (long-range transboundary air pollution, about 18 %), Sewerage (effluents and waste water treatment sludge, about 3%) and Waste management sector (about 0.8%). Emissions of target substances from manufacture is not relevant in this report because there were poor information and data from this sector in Russia.

The most important pollutants from target substances are Cadmium, OPE, NPE, NP, SCCPs, PBDEs and Mercury putting together almost 100% (99,4%) by mass from yearly load of BSAP substances in St.-Petersburg and Leningrad Region. Total yearly load of hexabromocyclododecane, perfluorooctanesulfonates/perfluorooctanesulfonic acid, tributyltins/triphenyltin, octylphenols and endosulfan (all together) could be evaluated as unsubstantial for target regions (<0.6% from summary load of target substances).

Estimated level of dioxins is comparatively low – about 44,5 g I-TEQ. Relevant source of dioxins in air is Energy production sector including househols (production of heat).

Due to the lack of reliable data and infromation concerning target substances in Russia the most part of estimations was made by scaling with EU data with big uncertainties (C). More or less bookworm information was found about mercury emissions.

3 References

Resolution №132 of Customs Union Commission EvrAzEC from 27.11.09 « On united nontariff regulation of Customs Union of Belarussia, Kazakhstan and Russian Federation». (www.alta.ru/taksa-online/goodinfo_out/2909303100).

Bulletin "Socio-economic situation of St.-Petersburg in 2010" http://petrostat.gks.ru

State report "Environment and environment protection in Russian Federation in 2009" www.mnr.gov.ru

Report on condition and use of the lands in Leningrad Region in 2009. Federal Agency of the Cadastre of Real Estate in Leningrad Region, 2010. http://www.to47.rosreestr.ru

Report of St.-Petersburg for Nature Use, Environmental Protection and Ecological Safety for 2009, p. 438

Report on condition and pollution of environment in Russian Federation in 2008. Russian Federal Service for Hydrometeorology and Environmental Monitoring (RosHydroMet) www.meteorf.ru

BaltHazar. Reduction of risks from hazardous waste in Russia. Final report. 2010. www.helcom.ru

Hazardous substances in industry. Guidance for engineers and chemical industry workers. 1976, p. 592

Ja.M. Grushko. Hazardous organic compounds in industrial waste water. Guidance. 1982, p. 216

Maximum permissible concentration of chemicals in environment. 1985, p. 528

Sanitary Norms and Rules 2.1.4.1074-01

Hygienic Norms 2.1.5.1315-03

GOST 12.1.005-88 General sanitary - hygienic requirements to working area air

Hygienic Norm 2.1.5.2280-07 "Maximum permissible concentration (MPC) of chemical substances in household, cultural and drinking water bodies"

Regulation of surface water protection from pollution by sewage, 12-04-11; Instruction of the Melioration and Water Management Ministry of the USSR from 16.05.74

Order N201 of the Committee on Municipal Facilities Management from 25.11.1996 (edited 26.08.2005), Chapter 4 “Waste water and pollutants prohibited for a discharge to sewerage system of St.-Petersburg”

Report ACAP “POPs in Arctic area of Russian Federation, 2009, http://npa-arctic.ru.

A. Treger, V. Rozanov, N. Krishtal, Br. Tikhonov, V. Rezepov. Inventory of PCBs and PCB-containing equipment and solutions to the problem of PCBs in the Russian Federation.// All-

Russian conference on the problem of persistent organic pollutants. 28-29.10.2002

Industrial production in St.-Petersburg and Leningrad Region in 2009, http://petrostat.gks.ru

GOST 17.1.3.04-82 Requirements for surface and ground waters protection from pollution of pesticides

SanPin 2.2.1/2.1.1.567-9 Sanitary Norms and Rules

Annual State catalogue of pesticides and agrochemicals allowed for the use in Russian Federation

Russian statistic yearbook, 2010

Water Quality Standards for Fishering basins, Order N20 from 18.01.2010, Federal Fishering Agency

GN 1.1.546-96 List of hygienic norms of pesticide contains in environmental objects

SFA Dioxins, Furans, Dioxin like PCB (Europe), draft ver.1, January, 2011

SFA PBDEs (EU27) Draft.ver.2, 09 May, 2010.

SFA Cadmium (EU27), ver.1-3, 12 July, 2011

SFA Endosulfan (EU27), draft ver.1.4, 2010.

SFA Nonylphenol etoxylates (EU27), version1.1, 23.June 2011

SFA Substance (EU27), Draft, 09 February 2011

Andersson H. SFA HBCDD, Draft ver.2, June 21 2010.

SFA Chloroalkanes C10-C13 (EU27), Draft vers.1.2, June 28 2010.

UNECE/CLRTAP Air emission inventories 2008, 15th March 2010 submission, http://cdr.eionet.europa.eu/lv/un/copy_of_colqhgwdg

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