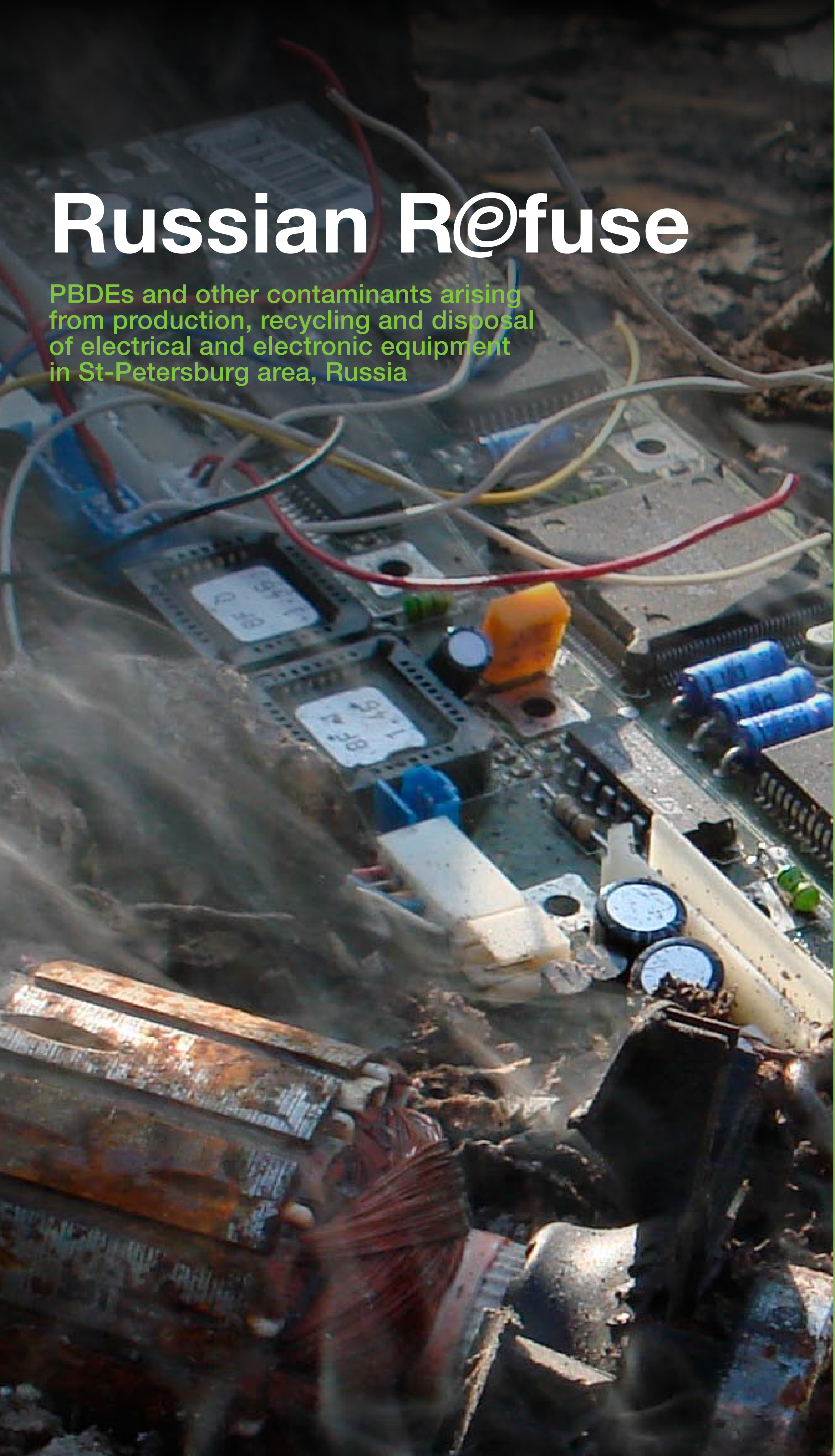

Russian R@fuse

PBDEs and other contaminants arising from production, recycling and disposal of electrical and electronic equipment in St-Petersburg area, Russia

GREENPEACE

greenpeace.org

Russian R@fuse

Cover/below: *E-wastes burning area near Novaya Derevnya railway station, Kolomyazhskiy prospect, St-Petersburg, Russia, 2007. © Greenpeace*

PBDEs and other contaminants arising from production, recycling and disposal of electrical and electronic equipment in St-Petersburg area, Russia

For more information contact:
isunit@diala.greenpeace.org

Authors:
Iryna Labunska
Kevin Brigden
David Santillo
Alexey Kiselev
Paul Johnston

Greenpeace Research Laboratories
Technical Note 07/2008

JN 156

Published in August 2008
by Greenpeace Research Laboratories
School of Biosciences
University of Exeter
Exeter EX4 4PS, UK
Tel: +44 1392 263917
Fax: +44 1392 423635
www.greenpeace.to

Contents

Executive Summary

1

E-wastes burning area located at the Obukhovskoy oborony prospekt, at the place where Murzinka River enters pipeline, St-Petersburg, Russia, 2007. © Greenpeace

Introduction

The City of St-Petersburg is located in the Leningrad Province of the Russian Federation, on the banks of the Neva River, which provides drinking water for its 5 million inhabitants. The city and its surroundings are home to a diverse array of industrial enterprises, including a substantial concentration of facilities engaged in the manufacture of electrical and electronic equipment. While the final products go to 'high tech' applications, the manufacturing processes employed can be very intensive in their use of hazardous chemicals, generating large quantities of wastes which, in the St-Petersburg area, are either discharged directly to the Neva River or directed to one of three large common effluent treatment plants. Solid wastes ('sludges') from treatment go to landfills, along with municipal and other wastes generated in the region. In addition, many poorer areas of the city itself are host to an unofficial and unregulated system of 'recycling' of electronic wastes ('e-wastes'), including the common and hazardous practices of open-burning of cables, circuit boards and other components in order to recover traces of precious metals for resale. Such activities may, in turn, act as significant sources of exposure of humans and the environment to hazardous chemicals and materials which are routinely incorporated into electrical and electronic goods at the manufacturing stage.

Taken together, these industrial and waste recycling/disposal activities represent a significant potential source of toxic and persistent pollutants to the Neva River and the City of St-Petersburg. Although there is some routine monitoring of water quality in the Neva basin, this covers a relatively small range of indicators measured in the water alone. As a result, information on the distribution and fate of contaminants such as heavy metals and persistent organic pollutants in the Neva River remains limited.

Aims of the current study

The current study was, therefore, designed as a first step towards addressing this shortfall, using the analysis of samples of industrial wastes, soils, sediments and river waters in order to provide a snapshot of contaminant inputs and environmental distribution in the St-Petersburg area. It does not, and was not intended to, represent a comprehensive description of either waste management practices or environmental quality in the region, but nonetheless provides some detailed analytical data, including for sediments in the Neva River, where such data have so far been lacking.

A total of 41 samples were collected during July and October 2007, including:-

- wastewater and associated sediment samples from several industrial sites located within St-Petersburg city,
- effluent and sludge samples from wastewater treatment plants (WWTPs) and landfills receiving wastes from the electronics sector, among many other sources,
- ash-contaminated soil samples from sites at which 'e-wastes' have been openly burned, and
- samples of river water and sediments from the Neva River basin around St-Petersburg, which ultimately receives wastewaters of various origin.

The results of this sampling programme are summarised below.

Manufacture of electrical and electronic goods

Wastewater discharged to the Okhta River from the company JSC "Electropult", which manufactures automated control systems, switches and semi-conductor equipment, contained high levels of cadmium, chromium, copper, nickel, tin and zinc, with cadmium present at 59 µg/l (parts per billion) and copper at 1450 µg/l. These substantial discharges of metals have led to their accumulation in river sediments close to the pipes, including cadmium concentrations ranging from 2.9 to 19.8 mg/kg (parts per million).

This same facility was also found to be discharging a range of volatile chlorinated organic compounds, including 36 µg/l of chloroform and 65 µg/l of the highly toxic tetrachloromethane, which is carcinogenic to animals and classed as possibly carcinogenic to humans.

Sediments collected from the Okhta River adjacent to the discharge pipes were also contaminated with a range of polybrominated diphenyl ethers (PBDEs), a group of persistent and toxic chemicals widely used as flame retardants, including in electrical and electronic goods. One of the sediment samples also contained well above trace levels of the obsolete and widely banned industrial chemicals polychlorinated biphenyls (PCBs), formerly used as flame retardants, insulating materials and even plasticisers and long recognised and regulated as persistent organic pollutants (POPs).

A sample of a single wastewater discharge apparently comprised of the combined effluents of a number of industrial units located on the Pirogovskaya Embankment contained a very diverse array of halogenated (chlorinated or brominated) and non-halogenated organic chemicals, including compounds used as flame retardants (PBDEs and chlorinated organophosphorus preparations), photoinitiators (including numerous derivatives of ketones and hydrazones), polymer additives (including the phthalate plasticiser DEHP), semiconductor coatings (quinoxaline derivatives) and chemical intermediates used in the pharmaceutical and bulk chemical sectors (including pyrazines and diphenylhydrazine). The presence in this sample of a compound commonly known as methyl centralite indicates significant inputs from explosives manufacture.

Effluent discharged from the JSC "Ladoga" facility, one of the biggest producers of civil and military hydro-acoustic equipment, among many other electrical and electronic products, contained between 58 and 77 µg/l of the chlorinated solvent chloroform. Sediment collected from the banks of the Neva River at the point of discharge was contaminated with PBDE flame retardants.

A sample of sediment collected from the inside of a pipe running from the the Petrogradskaya Embankment Industrial Estate (but not in operation at the time of sampling) contained a range of toxic organic compounds such as PBDEs, PAHs, and chlorinated benzenes. Levels of copper and zinc were approximately five times those typically found in uncontaminated freshwater sediments, and somewhat less elevated levels of cadmium and lead. This industrial estate houses several plants, including JSC "Vector Technology", which is involved in printed circuit board production and soldering.

Wastewater treatment plants and landfills

Effluent from the Northern combined wastewater treatment plant, which discharges 1250 million m3 of treated wastewater per day to the Gulf of Finland at Nevskaya Guba, appeared to contain relatively low levels of organic and heavy metal contaminants. In contrast, a sample of the sludge waste generated by the plant and taken to the Poligon Severny sludge disposal site was heavily contaminated with cadmium (51 mg/kg) and organic compounds. Among a total of 188 individual organic compounds isolated from this sample (of which only half could be identified with any degree of reliability) were 23 PBDE congeners (ranging from di- to deca-BDE), and a diversity of chlorinated benzenes and anilines, alkylbenzenes and organosilicon compounds. Far from destroying such persistent organic pollutants, therefore, conventional wastewater treatment plants simply transfer such pollution from one form to another and can exacerbate environmental problems in the vicinity of the sludge disposal sites. Indeed, a sample of sediment collected from a channel receiving runoff from the sludge disposal pits at the Poligon Severny site contained more than 100 organic compounds, including PBDEs, PCBs and PAHs. Both surface and groundwater collected from the same site contained, among other chemicals, the highly toxic nitrile compound 3-hexenedinitrile, otherwise known as 1,4-dicyano-2-butene.

The Central Wastewater Treatment Plant, located on Bely Island in the Nevskaya Guba, discharges approximately 1.5 million m3 of treated effluent per day, via a series of subsurface pipes with dispersive heads. Despite the high dilution which occurs as a result, a sample of water collected close to the pipes contained detectable levels of the solvent 1,2-dichloroethane, of chloroform, and of alkylphenol and benzothiazole derivatives.

Finally, leachate and associated sediments collected from the Southern municipal waste landfill, which covers an area of more than 58 hectares and receives a mixture of household and so-called ‘low toxicity’ industrial wastes, contained numerous PBDEs, chlorinated benzenes and, in the case of the sediment, a range of PCBs.

Sites used for open burning of e-wastes

Four samples of ash-contaminated soils, collected from a total of three separate sites within St-Petersburg used for unregulated open burning of electrical and electronic wastes, contained very high levels of copper, lead, zinc, antimony and, in some cases, tin, all metals commonly associated with components of electronic equipment. For example, lead was present at concentrations ranging from 3.8 to 5.6 grammes per kg (parts per thousand), i.e. up to half a percent of the total weight of the samples was lead. Concentrations of cadmium were also high, exceptionally so (250 mg/kg) in one of the four samples.

A range of persistent brominated and chlorinated organic compounds were also associated with these samples. All contained PBDEs and chlorinated benzenes, with variations in the patterns of PBDE congeners present from site to site probably reflecting differences in the types of e-waste processed. One sample contained PCBs, while another revealed the presence of chlorinated chemicals thought to be short-chain chlorinated paraffins, once widely used as flame retardants and plasticisers in electrical cables.

Although the contamination in soils on these sites which results from open burning of e-wastes may be seen to be localised and patchy, such highly contaminated ashes can act as a source of metal and organic pollutants to local residents and the surrounding environment, not least through wind-blown redistribution of ashes. In addition, the nature of contaminants remaining in the soils and ashes gives an indication of the types of pollutants which must also be released to the air when the wastes are being burned.

Waters and sediments from the Neva River

In addition to the more targeted sampling described above, samples of sediment and river water from the Neva River and its tributaries were collected at a total of six locations stretching from the river's origin in Lake Ladoga down to St-Petersburg itself. Although it is not possible from these samples to identify specific sources of pollution, especially as periodic flooding undoubtedly results in large-scale resuspension and redistribution of sediments along the length of the river, the results do indicate a significant background of environmental contamination with industrial chemicals, including PBDEs, PAHs and, in one case, PCBs. The metals copper, lead and zinc were also prominent at some sites along the Neva River. It is understood that, while local authorities do undertake some routine monitoring of water quality in the region, sediment quality has not been subject to the same level of scrutiny. As such, the results presented in this report may well represent some of the first published information on contaminant distribution.

Summary and recommendations

Overall, this 'snapshot' study has shown that environmental contamination of the Neva River basin with metals and persistent organic pollutants is a widespread and, in many cases, ongoing problem. Current inputs include both direct discharges from industrial facilities engaged in the manufacture of electrical and electronic equipment and effluents discharged indirectly to one of the large common wastewater treatment plants located around the city. Even where cleanup of the wastewater is apparently being effective at removing such contaminants from the effluent finally disposed of to sea, evidence suggests that this is simply creating additional hazardous waste streams in the form of sludges, which are adding to the legacy of pollution in landfills and sludge disposal sites. At the same time, the dangerous and unregulated practice of open burning of electrical and electronic wastes to recover precious metals, commonplace in several areas of St-Petersburg, is generating further hotspots of contamination with toxic and environmentally persistent pollutants.

Greater monitoring and control of the generation and disposal of industrial wastes in the St-Petersberg region are clearly urgent priorities for protection of the environment and, ultimately, of the supplies of drinking water on which the city depends. This study serves as an indication of the diversity and scale of contaminant releases, which can be used in the first instance to target further study and identification of point sources of pollution. In that way, the problems identified here can begin to be tackled more effectively through measures taken at source, such as through the implementation of clean production techniques and the replacement of hazardous processes, chemicals and materials with safer alternatives. Ultimately, such approaches are far more sustainable, in environmental, social and economic terms, than continuing to generate huge volumes of contaminated water and solids which simply move pollution from one environmental compartment to another.

In relation to the manufacture and recycling or disposal of electrical and electronic equipment, recent and ongoing legislative developments within the European Union (in the form of the WEEE and associated RoHS Directives) have led to substantial steps forward in avoiding the use of hazardous chemicals such as lead, cadmium and PBDEs in such products, reducing the impacts of all stages in their lifecycle and making take-back and proper recycling of obsolete equipment more and more feasible. The development of equivalent controls within Eastern Europe, including in the Russian Federation, would clearly be a justifiable and highly effective contribution to tackling the growing environmental and health burdens of the electronic age.

Introduction

2

Effluent pipe located in front of JSC "Ladoga", discharging into the Neva River, St-Petersburg, Russia, 2007. © Greenpeace

The problem of environmental pollution caused by the production, recycling and disposal of electronic and electrical goods has been known for some time. There are numerous studies reporting the release of toxic compounds during these processes, such as lead, cadmium, copper, nickel, brominated flame retardants, polychlorinated biphenyls (PCBs), and other compounds including chlorinated solvents. Concerns about the growing amount of obsolete electronic and electrical equipment, also known as 'e-waste', led the European community to adopt two pieces of legislation aimed at addressing the problem, namely the Directive on Waste Electrical and Electronic Equipment (WEEE), and that on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS). These directives require, among other things, that Member States take responsibility for ensuring that equipment manufacturers set up systems for treatment and recovery of electrical and electronic waste, as well as placing prohibitions on the use of certain hazardous substances (most uses of lead, cadmium, mercury and chromium (vi), as well as some brominated flame retardants such as PBDEs) in the manufacture of electrical and electronic goods.

However, beyond the European Union, few countries have equivalent regulations and, as a result, have limited controls to ensure safe and environmentally sustainable recycling and disposal of e-wastes. In order to obtain information on the consequences of this lack of regulatory controls, Greenpeace has in the past conducted studies to investigate workplace and environmental contamination due to e-waste recycling activities in China and India (Brigden *et al*. 2005 & 2006) as well as to document current practice in chemical waste discharges from the electronics manufacturing industry in China, Thailand, Philippines and Mexico (Brigden *et al*. 2007).

The current study was undertaken to investigate environmental contamination caused by production of electronics, and also by recycling and disposal of e-wastes, in the Leningrad district of Russia, with a specific focus on the city of St-Petersburg, located on the banks and delta of the Neva River. The Neva River is 75 km long, and is the only river that starts from Ladoga Lake and enters Nevskaya Guba (part of the Gulf of Finland). About 6 km before its mouth, the Neva River divides into 5 branches, forming the river delta. Despite its modest length, the Neva is the third largest river in Europe in terms of average discharge (after the Volga and the Danube), with a catchment straddling several countries, including Russia, Finland and Belarus. The Neva River supplies St-Petersburg city and its 5 million inhabitants with all its drinking water.

The majority of electronics manufacturers in St-Petersburg discharge their wastewaters into combined collection systems and the wastes undergo treatment at one of the three Waste Water Treatment Plants (WWTPs). However, some electronics companies continue to discharge their wastewaters directly into the Neva River or its tributaries and it is unknown if those wastewaters receive any prior treatment.

The Russian Federation in general, and St-Petersburg in particular, has no 'take–back' system for obsolete electronics. The local environmental authority, St-Petersburg's Committee on the Management of Natural Resources, Environmental Protection and Ecological Safety, has stated in a private communication (in response to a member of public who enquired about official way of domestic electrical equipment disposal) that they have no information about the presence of hazardous substances in obsolete household electronics which would require utilization of special facilities. Therefore, according to the Committee, the methods of treatment for such type of wastes do not differ from common practices employed for municipal solid wastes (Private Communication 2007). Thus, the most of electronic wastes generated in the city go to landfill or are collected from private backyards by well organised but unofficial waste pickers. After collection, these wastes are manually dismantled, sometimes even on the landfills, with certain components being burned in order to recover precious metals or simply buried on the landfills.

Based on this information, and on experiences with wastes management in the electronics sector in other parts of the world, it was considered valuable to conduct a 'snapshot' investigation in order to detect and identify priority pollutants arising from the electrical and electronic goods production, recycling and disposal sectors in St-Petersburg city and the surrounding area. 41 samples in total were collected over periods in July and October 2007, including:-

- wastewater and associated sediment samples from several industrial sites located within the St-Petersburg city,
- wastewater and sludge samples from WWTPs and landfills where obsolete electronics are routinely disposed,
- soil samples from sites at which e-wastes have been openly burned, and
- samples of river water and sediments from the Neva River basin around St-Petersburg, which ultimately receives wastewaters of various origin.

Sampling program

3

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Wastewater, ground water and river water samples were collected in a 1 litre screw-cap bottles. A Molchanov bathometer was used to collect river water samples. For those water samples analysed for volatile organic chemicals, a sample was also collected directly into separate 20 ml auto sampler crimp top vials (four vials per sample). Sediment, sludge and soil samples were collected in 100ml screw-cap bottles. All samples were kept cool and dark, and were returned to the Greenpeace Research Laboratories (University of Exeter, UK) for analysis. Detailed descriptions of sample preparation and analytical procedures are presented in the Appendix. Locations of the sampling sites are presented in Figure below.

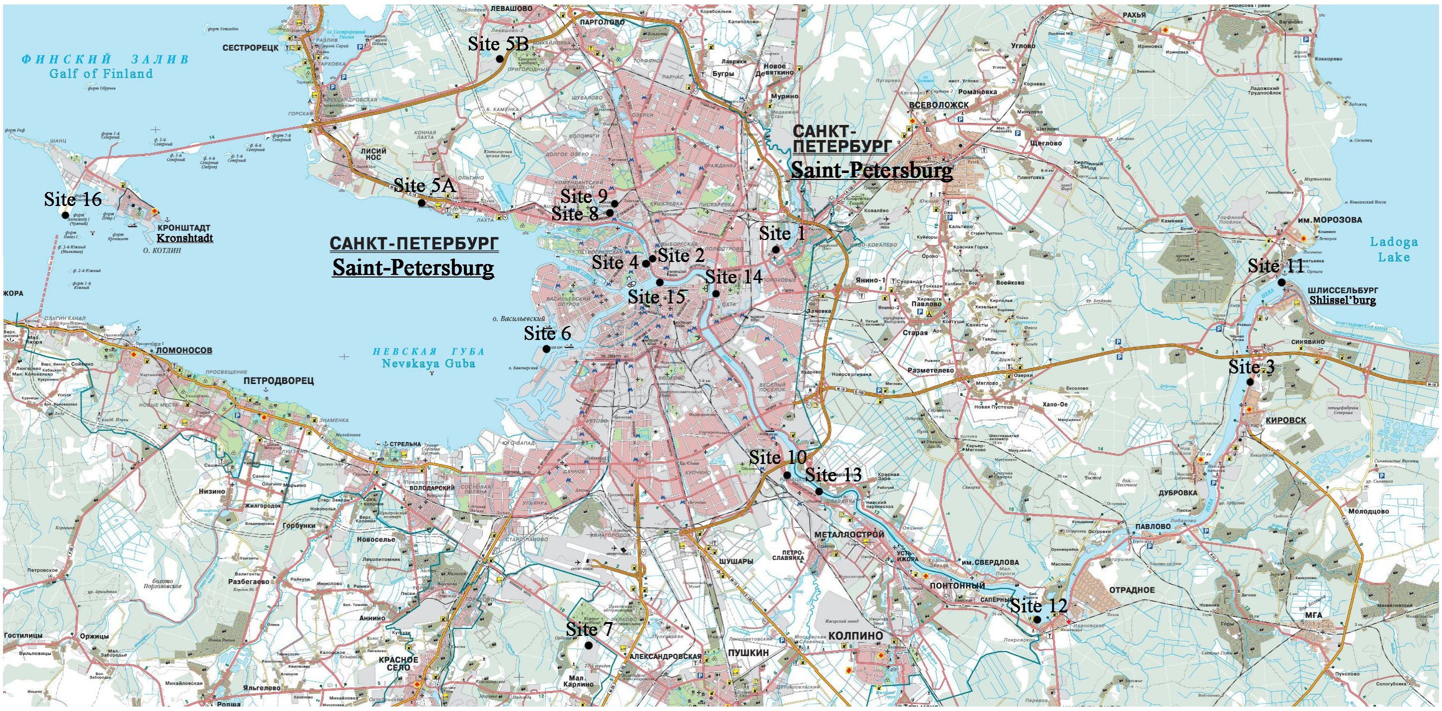

Fig. Location of the sampling sites, St-Petersburg, Russia, 2007.

Wastewater sampling from 1st effluent pipe located in front of JSC "Electropult", discharging into the Okhta River, St-Petersburg, Russia, 2007. © Greenpeace

3.1 Samples associated with electronic and electrical goods production

Ten samples associated with electronic and electrical goods production were collected from four industrial sites in St-Petersburg area in July and October 2007. These sites included two individual plants, JSC “Electropult” and JSC “Ladoga”, and two industrial zones located in the St-Petersburg city centre, on Pirogovskaya and Petrogradskaya embankments. Facilities located on Pirogovskaya embankment industrial zone included “Zavod Mezon”, “Zavod Russkiy Disel” and “ Zavod Dvigatel”. Among the plants located on Petrogradskaya embankment industrial zone is JSC “Vector Technology”. These sites were chosen on the basis of the known direct input of wastewater from the industrial facilities into the Neva River or its tributary, the Okhta River. Description of samples and sampling sites are presented in Table 1 and in the following text.

3.1.1. Site 1 - JSC “Electropult”

JSC “Electropult” is located on the banks of the Okhta River, which is the most contaminated tributary of the Neva River according to latest environmental reports produced in 2005-2006 by the local environmental committee and local hydro meteorological service (CNREP 2006). The Electropult facility manufactures products such as automated control systems, switches, semi-conductor frequency converters and low voltage equipment. Wastewaters from the territory of the plant are discharged via underground pipes directly into the Okhta River. Two such discharge pipes were located along the Okhta River in this location, identified here as discharge 1 and, in close proximity but further downstream, discharge 2. Samples of wastewater were collected from both pipes, as well as sediments in the immediate vicinity of these discharges. For the second discharge, samples were collected on two separate occasions, firstly in July 2007 (RU07011-RU070012) and secondly in October 2007 (RU 07039).

Site Nr.	Sample Code	Sample Type	Sampling date	Description of the sample source
Site 1	RU 07009	waste water	02.07.07	1st effluent pipe located in front of JSC “Electropult”, discharging into the Okhta River
	RU 07010	sediment	02.07.07	Okhta River by the 1st effluent pipe located in front of JSC “Electropult”
	RU 07011	waste water	02.07.07	2nd effluent pipe located in front of JSC “Electropult”, discharging into the Okhta River
	RU 07012	sediment	02.07.07	Okhta River by the 2nd effluent pipe located in front of JSC “Electropult”
	RU 07039	waste water	15.10.07	Same as RU 07011
Site 2	RU07022	waste water	04.07.07	effluent pipe in front of Pirogovskaya embankment industrial zone, discharging into the Neva River
Site 3	RU 07033	waste water	05.07.07	effluent pipe located in front of JSC “Ladoga”, discharging into the Neva River
	RU 07034	sediment	05.07.07	small canal formed by the effluent coming from the pipe located in front of JSC “Ladoga”, this canal goes directly into the Neva River
	RU 07043	waste water	16.10.07	Same as RU07033
Site 4	RU07023	sediment	04.07.07	sample was taken from inside on non-operated pipe located in front of Petrogradskaya embankment industrial zone

Table 1. Description of the samples collected in association with electronic and electrical goods production, St-Petersburg, Russia, 2007.

3.1.2 Site 2 - Pirogovskaya embankment industrial zone

The Pirogovskaya embankment industrial zone is located close to the city centre on the banks of the Neva River. There are several plants operating in this area, including “Zavod Mezon”, “Zavod Russkiy Disel” and “Zavod Dvigatel”. “Zavod Mezon” produces a wide range of electrical goods including capacitors, accumulators, and high voltage fuses. In the past, this plant used to produce television sets. “Zavod Russkiy Disel” is engaged in heavy engineering, electrical engineering and vehicle engineering, including manufacture of diesel engines and diesel-generator sets.   “Zavod Dvigatel” produces a range of submarine weapons for the Russian Navy, including universal self-guided torpedoes, mines, devices of hydro-acoustic counteraction for defence of submarines, among others. There is one combined wastewater discharge from the whole of this industrial zone, once again going directly to the Neva River. This discharge was sampled in July 2007 (sample RU 07022). It was not possible to collect any sediments in the vicinity of this discharge as the banks of the river at this location are concrete with stones on the riverbed.

3.1.3 Site 3 - JSC “Ladoga”

JSC “Ladoga” is located in the town of Kirovsk, in the Leningrad area near St-Petersburg. The plant was built in 1967 and remains one of the biggest producers of hydro-acoustic equipment for the Russian Navy, as well as producing civil consumer products such as marine radars, underwater communication equipment, training systems and other electronic and electrical products for energy, petrochemical and transport services. Another separate company, operating production lines for printed wiring (circuit) boards (PWBs), leases land within the territory of the Ladoga plant.

One discharge was identified as originating from the territory of this plant, carried via an underground pipeline, with the outfall a few meters from the Neva River bank, forming a small channel which finally joints the river. Two samples of wastewater were taken from this discharge, first in July (RU07033) and second in October (RU07043). The latter sample was subject to Volatile Organic Compounds (VOCs) analysis only. A single sample of sediment (RU07034) was also collected in July 2007 from the small channel formed by the powerful wastewater discharge observed at that time.

3.1.4 Site 4 - Petrogradskaya embankment industrial zone

Petrogradskaya embankment industrial zone is located on the bank of the Neva River within the city of St-Petersburg. There are several plants operating in this zone, including JSC “Vector Technology”, which maintains various types of printed circuit board production and soldering lines. One operating wastewater discharge pipe was identified from this industrial zone in June 2007, with the output directly into the Neva River. However, at the time of sampling in July 2007, no discharge was observed from this pipe. Thus, only single sediment sample (RU07023) was collected from inside the pipe.

3.2 Samples associated with WWTPs and landfills

The City of St-Petersburg has three main Waste Water Treatment Plants (WWTPs) - Central, Northern and South-Western, which together receive 80 % of city wastewaters from both households facilities and industrial plants. Samples were taken from two of these WWTPs, Central and Northern, as well as of materials associated with the Southern municipal waste landfill, one of the biggest in the St-Petersburg area. Full descriptions of the samples and sampling sites are presented in Table 2 and in the following text.

	Sample Code	Sample Type	Sampling date	Description of the sample source
Site 5A	RU 07014	waste water	03.07.07	Northern WWTP treated water underground pipeline, sample taken from a manhole in this pipeline about 10m deep, located in Olgino village, appr. 200m from the Nevskaya Guba, Gulf of Finland, where pipeline has underwater outlet
Site 5B	RU 07018	sludge	04.07.07	sludge slime pit of Northern WWTP, Poligon Severny
	RU 07019	ground water	04.07.07	control borehole appr. 1.5m deep at Poligon Severny
	RU 07020	leachate/ surface water	04.07.07	drainage canal between sludge slime pit of Northern WWTP located on Poligon Severny and a municipal waste landfill
	RU 07021	sediment	04.10.07	drainage canal between sludge slime pit of Northern WWTP located on Poligon Severny and a municipal waste landfill
	RU 07041	ground water	16.10.07	control borehole appr. 1.5m deep at Poligon Severny (same place as RU07019)
Site 6	RU 07015	waste water	03.07.07	underwater effluent dispersing pipe of Central WWTP, appr. 7m water depth, located at Nevskaya Guba, Gulf of Finland
Site 7	RU 07024	leachate/ surface water	04.07.07	swamp located between old and new parts of Southern municipal waste landfill
	RU 07025	sediment	04.07.07	swamp located between old and new parts of Southern municipal waste landfill
	RU 07040	leachate/ surface water	15.10.07	swamp located between old and new parts of Southern municipal waste landfill (same place as RU07024)

Table 2. Description of the samples collected in association with WWTPs and waste landfills, St-Petersburg, Russia, 2007.

3.2.1 Site 5A and 5B - Northern WWTP and Poligon Severny

The Northern WWTP, located in the village of Olgino near St-Petersburg, receives waste water from all facilities of St-Petersburg city that are located on the right-hand bank of the Neva River. This treatment plant produces 1,250 million cubic meters of treated waste water per day, which is discharged into the Nevskaya Guba, Gulf of Finland, via an underground and (when it reaches the coastline) underwater pipeline. A single sample of treated wastewater (RU07014) was collected from the underground pipeline by accessing a manhole located approximately 200m before the discharge reaches the Nevskaya Guba coastline.

Sludges generated by the Northern WWTP are transported for disposal to the sewage sludge landfill called Poligon Severny (property of Vodokanal Company, St-Petersburg), in operation since 1986. Poligon Severny contains four sewage sludge fields and storage for dry sewage sludge accumulation. There are control boreholes available for ground water contamination monitoring. Five samples in total were collected from the Poligon Severny in July and October 2007: sludge sample RU07018 from the sludge slime pit; leachate (RU07020) and sediment (RU 07021) samples from the drainage canal between the municipal waste landfill and sludge slime pit; and two samples of ground water collected from one of the control boreholes located at the Poligon Severny, the first in July (RU07019) and the second in October 2007 (RU 07041). The latter sample was subject to VOCs analysis only.

3.2.2 Site 6 - Central WWTP

The Central WWTP is located on Bely Island in the Nevskaya Guba (Gulf of Finland) and receives industrial and municipal waste water from all facilities located on the left bank of the Neva River. It produces 1.5 million cubic meters of treated waste water per day, which discharges underwater directly into Nevskaya Guba via series of pipes which have dispersive heads. A single sample of wastewater (RU07015) was collected by a diver from one of these dispersive heads, located about 7m beneath the surface. It was not possible to collect a sediment sample from the vicinity of the discharges as the bed of the Nevskaya Guba is mainly covered in sand and stones in this region.

3.2.3 Site 7 - Southern municipal waste landfill

The Southern municipal waste landfill (or PTO-1), which was constructed in 1978, is used for disposal of household and 'low toxicity' industrial wastes. It covers an area of 58.36 hectares and receives 2.4 million cubic meters of wastes per year, 98 % of which comes from St-Petersburg (representing 30% of all solid wastes produced by the city). Officially, this is the biggest landfill for St-Petersburg. Part of the landfill (23.5 hectares) is located on a hill about 30-35 meters high and it is here that wastes are currently disposed. At the bottom of the hill is a swamp, located between the new and the old, partly re-cultivated, parts of the landfill. Three samples were collected from the swamp, which apparently receives landfill leachate: a sediment sample RU07025, and two samples of swamp water/leachate, RU07024, collected in July, and RU07040, collected in October 2007. The latter sample was subject to VOCs analysis only.

3.3 Samples associated with e-wastes open burning sites

There are several sites in the St-Petersburg area where systematic open air burning of electronic wastes is taking place. Several such sites were identified and sampled in October 2007. Site descriptions and sampling details are given in Table 3 and in the following text.

Site Nr.	Sample Code	Sample Type	Sampling date	Description of the sample source
Site 8	RU07035	soil	02.07.07	small e-wastes burning area, about 3 square meters, near 20 Chernaya River embankment
Site 9	RU07036	soil	02.07.07	large e-wastes burning area near Novaya Derevnya railway station, Kolomyazhskiy prospect
Site 10	RU07037	soil	02.07.07	large concrete e-wastes burning area located at the 279 Obukhovskoy oborony prospekt, at the place where Murzinka River enters pipeline
	RU07038	soil	02.07.07	large e-wastes burning area located at the Obukhovskoy oborony prospekt, near Murzinka River and partially constructed wall of the WWTP

Table 3. Description of the samples collected from electronic wastes open air burning sites, St-Petersburg, Russia, 2007.

3.3.1 Site 8 - Naberezhnaya Chernoy Rechki

A small area used for the open burning of e-wastes was found near 20 Chernaya Rechki embankment. At this site, a range of different electronic components, as well as cables, were observed burning. Soil sample RU07035 was taken from the centre of a typical 'fire pit'.

3.3.2 Site 9 - Kolomyazhskiy prospekt

A relatively large area of e-waste burning was found near Novaya Derevnya railway station on Kolomyazhskiy prospect, a known area of residence for many permanently homeless people, some of whom are engaged in burning e-waste to recover precious metals. Household wastes and elements of destroyed and burned metal-like objects are commonplace here. Sample RU07036 was collected from a typical 'fire pit' within this large open burning site.

3.3.3 Site 10 - Obukhovskoy oborony prospekt

Two places used for the open air burning of e-wastes were identified at the Obukhovskoy oborony prospekt. The first of these had a concrete base, covered with a thin layer of soil but devoid of grass or other vegetation. Partially burned cables were widely scattered here. A sample of soil (RU07037) was collected from the centre of a typical 'fire pit', located 250 m east from the point at which the Murzinka River enters an underground pipe. The second area used for e-waste burning was located nearby, on the left bank of Murzinka River by the wall of a partially constructed waste water treatment facility. Residues of burned cables were also very common here. Soil sample RU07038, which was visually rich in organic matter, was collected from the centre of a typical 'fire pit'.

3.4 Environmental samples - Sites 11-16

In addition to those samples described above, a total of 17 samples were collected from six sites along the Neva River in July 2007 in order to give an indication of the extent of environmental contamination to which industrial and municipal waste disposal are contributing. These environmental samples include 6 water and 11 sediment samples, collected from locations starting from the river's origin near Orekhoviy Island on Ladoga Lake and ending near Fort Konstantin just before the dam on the St-Petersburg sea canal. Water and sediment samples were also taken before and after the inflow of the main Neva River tributaries – the Tosna, Slavyanka and Okhta Rivers. Sites descriptions and sampling details are given in Table 4 below.

Site Nr.	Sample Code	Sample Type	Sampling date	Description of the sample source
Site 11	RU 07026	river water	04.07.07	riverhead of the Neva River, near the Buoy Nr.58 fairway, next to Orekhoviy Island, Ladoga Lake
	RU 07027	sediment	04.07.07	riverhead of the Neva River, near the Buoy Nr.58 fairway, right bank of the river, in the vicinity of the wharf
	RU 07028	sediment	04.07.07	left bank of the Neva River, 1.5km downstream from Orekhovy Island, Shlisselburg
Site 12	RU 07031	sediment	04.07.07	Neva River, about 3m from the left bank, downstream of junction with Tosna River, 45cm water depth
	RU 07032	river water	04.07.07	Neva River, about 40m from the left bank and 500m downstream of junction with Tosna River, 1.5m water depth
Site 13	RU 07029	river water	04.07.07	Neva River, about 20m from the left bank and 500m downstream from the junction with Slavyanka River
	RU 07030	sediment	04.07.07	left bank of the Neva River, 1km upstream of the Guyed Bridge, downstream of Slavyanka River
Site 14	RU 07001	river water	02.07.07	Okhta River junction with the Neva River, under the Bolsheokhtinsky bridge crossing Okhta River
	RU 07004	sediment	02.07.07	Okhta River junction with the Neva River, under the Bolsheokhtinsky bridge crossing Okhta River
	RU 07002	sediment	02.07.07	Neva River, 3-5m from the bank, about 10m downstream of the Bolsheokhtinsky bridge, 5m water depth
	RU 07003	sediment	02.07.07	Neva River, about 500m downstream of the Bolsheokhtinsky bridge, Sverdlovskaya embankment
Site 15	RU 07005	river water	02.07.07	Neva River by the 2nd pier of Liteyniy Bridge, water depth 1.5m
	RU 07006	sediment	02.07.07	Neva River,close to the left bank, just downstream of Liteyniy bridge, near to staircase leading to river
	RU 07007	sediment	02.07.07	Neva River, close to the right bank, just downstream of Liteyniy bridge
	RU 07008	sediment	02.07.07	Bolshaya Nevka River (side branch of Neva River), in the vicinity of the Aurora ship
Site 16	RU 07016	river/sea water	03.07.07	Nevskaya Guba, Gulf of Finland, several meters offshore, next to the sea canal
	RU 07017	sediment	03.07.07	Nevskaya Guba, Gulf of Finland, about 0.5m offshore

Table 4. Description of the samples collected from the Neva River basin, St-Petersburg, Russia, 2007, from upstream (site 11) to downstream (site 16).

Methodology

4

Underwater effluent dispersing pipe of Central WWTP, located at Nevskaya Guba, Gulf of Finland, St-Petersburg, Russia, 2007. © Greenpeace

A range of different analyses was carried out on the various samples collected, depending on the sample type. A summary of the type of analyses for each group of samples is given below.

Heavy metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. A wide range of metals and metalloids were quantified in all samples, the list being based on their known use in the electronics sector and their previously reported presence in e-waste recycling yards (Brigden *et al*. 2005, Brigden *et al*. 2007).

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), following liquid:solid extraction into a mixture of pentane and acetone (for solid samples) or liquid:liquid extraction with pentane only (for water and wastewater samples). Volatile organic chemicals (VOCs) were identified and quantified in water samples without extraction or pre-treatment, using GC/MS with HeadSpace sample introduction technique.

More information on the methods of analysis for organic compounds, metals and metalloids is provided in the Appendix.

Sample type	**Type of analysis**		
	Metals (quantitative)	Extractable organic compounds (qualitative)	Volatile organic compounds (qualitative & quantitative)
Groundwater	√	√	√
Wastewater	√	√	√
River water	√	√	-
Sediment	√	√	-
Sludge	√	√	-
Soil	√	√	-

Results and discussion

5

Sediment sampling by the 1st effluent pipe located in front of JSC "Electropult", discharging into the Okhta River, St-Petersburg, Russia, 2007. © Greenpeace

The results for the qualitative screening analysis for extractable organic compounds, quantitative analysis for VOCs and quantitative analysis for heavy metals are presented in the following paragraphs 4.1 – 4.4, according to the origin of the samples.

5.1 Samples associated with electronic and electrical goods production

Analytical results for samples associated with electronic and electrical goods production in the St-Petersburg area are presented in Tables 5 (heavy metals), 6 (extractable organic compounds - qualitative analysis only) and 7 (quantitative VOCs analysis).

5.1.1 Site 1 - JSC "Electropult"

In total, five samples were collected from Site 1 - JSC "Electropult", including two sediment samples (RU07010 and RU07012) and two wastewater samples (RU07009 and RU07011) collected in July and one wastewater sample (RU07039, for VOCs analysis only) collected in October from the same location as sample RU07011.

Location	Site 1				Site 2	Site 3		Site 4
	1st pipe		2nd pipe					
Sample Code	RU07009	RU07010	RU07011	RU07012	RU07022	RU07033	RU07034	RU07023
Sample type	**WW**	**SED**	**WW**	**SED**	**WW**	**WW**	**SED**	**SED**
	(µg/l)	(mg/kg)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<20	<20	<20	<20	<20	<20	<20	<20
Barium	86	194	129	217	28	27	50	186
Beryllium	<2	0.2	<2	0.2	<2	<2	<0.2	<0.2
Bismuth	<20	<20	<20	<20	<20	<20	<20	<20
Cadmium	<5	2.9	59	19.8	<5	<5	<0.5	1.8
Chromium	<20	53	504	36	<20	<20	16	42
Chromium (VI)	n/a	n/a	<50	n/a	n/a	n/a	n/a	n/a
Cobalt	329	294	<20	4	<20	<20	4	3
Copper	<20	175	1450	143	<20	<20	21	200
Gallium	<20	<20	<20	<20	<20	<20	<20	<20
Germanium	<30	<30	<30	<30	<30	<30	<30	<30
Indium	<20	<20	<20	<20	<20	<20	<20	<20
Iron	4480	n/a	3660	n/a	440	813	n/a	n/a
Lead	<50	59	<50	30	<50	<50	17	69
Manganese	1010	548	767	283	61	87	191	91
Mercury	<0.5	1.9	<0.5	0.2	<0.5	<0.5	<0.1	0.1
Molybdenum	<20	5	<20	<2	<20	<20	<2	<2
Nickel	44	199	520	20	<20	<20	7	15
Selenium	<50	<30	<50	<30	<50	<50	<30	<30
Tin	<50	<10	70	34	<50	<50	<10	16
Vanadium	<20	16	<20	11	<20	<20	13	9
Yttrium	<10	4	<10	5	<10	<10	6	4
Zinc	66	664	2230	220	49	21	47	561

Table 5. Metals identified in wastewater (WW) and sediment (SED) samples from industrial sites with electronic and electrical goods production, St-Petersburg, Russia, 2007. n/a – not analysed.

The discharge of metals in wastewaters was evident for both pipes, though to a far greater extent for the 2nd pipe. Wastewater from the 2nd pipe (RU07010) contained many metals at high concentrations, including cadmium, chromium, copper, nickel, tin and zinc. Cadmium and copper concentrations were particularly high, both at over 50 times typical background levels for surface waters, while nickel and zinc levels in the wastewater were around 20 times higher than typical background. Though the wastewater contained a high level of chromium, the most toxic form (known as chromium VI or hexavalent chromium) was not present above the detection limit.

High concentrations of certain metals (cadmium, copper and zinc) were also found in river sediments in the vicinity of the the two pipes (RU07010 and RU07012), suggesting their accumulation over time due to ongoing discharges of contaminated wastewaters at this location. Both the wastewater from the 1st pipe and the sediments in the vicinity (RU07009 and RU07010) contained unusually high levels of cobalt. However, the elevated levels of other metals, such as cadmium, copper, mercury, nickel and zinc, detected in sample RU07010 may reflect more the inputs from the 2nd pipe, located approximately 5m downstream along the slow flowing river, than those from the 1st pipe.

Location	**Site 1**				**Site 2**	**Site 3**		**Site 4**
Sample Code	RU07009	RU07010	RU07011	RU07012	RU07022	RU07033	RU07034	RU07023
Sample type	**WW**	**SED**	**WW**	**SED**	**WW**	**WW**	**SED**	**SED**
No. of organic compounds isolated	103	295	112	246	278	97	99	151
No. of reliably identified compounds (% of total)	29(28%)	121(41%)	29(26)	27(11%)	72(26%)	25(26%)	20(20%)	56(37%)
Halogenated VOCs	2(3)	n/a	(2)	n/a	(1)	1(1)	n/a	n/a
PBDEs	-	(14)	-	(6)	(5)	-	(7)	(11)
PCBs	-	61(4)	-	-	-	-	-	-
Chlorinated benzenes	-	-	-	-	-	-	(1)	(2)
Chlorinated anilines	-	-	-	-	3	-	-	-
Phthalate esters	3	1	-	-	1	2	-	-
Fatty acids and derivatives	3	-	1	-	2	-	-	-
PAHs	-	19	-	6	2	-	3	16
Alkyl benzenes	-	-	-	-	-	-	-	4
Substituted ketones/ hydrazones	-	-	-	-	11	-	-	-
Substituted amines/amides	-	-	-	-	2	-	-	-
Terpenoids	-	-	-	-	3	-	-	-
Substituted phenols	1	-	-	-	3	-	-	-
Nonylphenyl(di-nonyl)phenyl amine isomers	-	-	2	-	-	-	-	-
Sterol derivatives	-	-	-	-	1	-	1	1
Diphenylhydrazine	-	-	-	-	1	-	-	-
Methyl centralite	-	-	-	-	1	-	-	-
Fyrol PCF isomers	-	-	-	-	2	-	-	-
Sulphur	1	-	-	-	1	-	-	-
Alkanes & alkenes	15	18	25	15	19	20	6	19
Heterocyclic aromatic compounds	-	-	-	-	9	-	-	1
Other hydrocarbons	1	4			6	1	2	2

Table 6. Organic chemicals identified in wastewater (WW) and sediment (SED) samples from industrial sites with electronic and electrical goods production, St-Petersburg, Russia, 2007. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; n/a – not analysed; (-) – not detected.

Box 1. Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are one of several classes of brominated compound in widespread use as flame retardant additives in plastics and foams, including plastic casings of electronic equipment (OECD 2003). There are many different chemicals (congeners) included in this group, differing in the numbers and positioning of bromine atoms in the molecules. Those in common commercial use are “penta” (i.e. a mixture rich in pentabrominated congeners), “octa”, (rich in octabrominated congeners) and “deca” (almost exclusively the decabrominated congener).

PBDEs are environmentally persistent chemicals. Some, especially the lower brominated congeners (e.g. “penta-BDE”), are also highly bioaccumulative. Their manufacture and use as additives in plastics and other polymers, in which they are not tightly bound to the polymer matrix, has led to their widespread presence in the environment. PBDEs can be detected in indoor air and dusts in the workplace and in the home (Santillo *et al*. 2003 a & b). They also occur in almost every part of the environment, including sediments (Allchin & Morris 2002), freshwater and marine fish (Asplund *et al*. 1999a, b), birds eggs (Hites 2004) and even whales from the deep oceans and the Arctic (de Boer *et al*. 1998, Ikonomou *et al*. 2002).

PBDEs have also been reported as common contaminants in humans, including reports from Sweden, Spain, Finland and North America (Lindstrom *et al*. 1997, Meneses *et al*. 1999, Strandman *et al*. 1999, She *et al*. 2000). Concentrations of lower brominated PBDEs have shown increasing levels in both blood and breast milk in recent decades, particularly in regions in which “penta” remains in commercial use (Alaee *et al*. 2003, Meironyte *et al*. 1999, Thomsen *et al*. 2002). Workers in electronics recycling facilities in Europe have been found to have higher blood levels of PBDEs than other workers, probably as a result of inhalation of contaminated dust (Sjödin *et al*. 2001, Sjödin *et al*. 2003). Similarly, elevated levels have been reported in the blood of workers (Qu *et al*. 2007) and local residents (Bi *et al*. 2007) at an e-waste recycling area in China. For the general population, exposure to PBDEs probably occurs through a combination of food contamination and direct exposure to chemicals from consumer products and/or contaminated dusts (Harrad *et al*. 2004). While their acute toxicity is considered low, chronic exposure to certain PBDEs (especially in the womb) has been associated with abnormal brain development in animals (Eriksson *et al*. 2002), with possible long-term impacts on memory, learning and behaviour (Darnerud 2003, Eriksson *et al*. 2001, 2002, Viberg *et al*. 2004). There are concerns that similar effects may be of relevance in humans (Branchi *et al*. 2003). PBDEs also exhibit endocrine (hormone) disrupting properties, interacting with both oestrogen and thyroid hormone systems either as the parent compound or as metabolites (Meerts *et al*. 1998, 2001, Legler & Brouwer 2003). Effects on the immune system have also been reported (Birnbaum & Staskal 2004, Darnerud 2003). Furthermore, when plastics containing PBDEs are burned, either in an incinerator or by open burning, the potential exists for formation of brominated dioxins (IPCS 1998) and mixed halogenated dioxines, which may be of equivalent or even greater toxicity to chlorinated dioxins (Olsman *et al*. 2007).

Because of these environmental and human health concerns, controls are increasingly being placed on the use of PBDEs (along with some other brominated fame retardants) in some regions. Penta-BDE is included as a “priority hazardous substance” under the EU Water Framework Directive (EU 2001) and remains under consideration for inclusion as a POP (persistent organic pollutant) under the 2001 global Stockholm Convention (Peltola & Yla-Mononen 2001, UNEP 2006). Both “penta” and “octa” are now banned from use in Europe (EU 2003a). Within the electronics sector, use of PBDEs other than “deca” was prohibited from July 2006 under the Directive on Restrictions on Hazardous Substances (RoHS), associated with the WEEE Directive (EU 2002a, b). However, the European court ruling has removed the exemption for deca BDE from the Annex to the RoHS Directive from 1 July 2008.

The pattern of organic compounds detected in wastewater samples from the 1st and 2nd pipes was slightly different (see Table 6), possibly due to wastewater streams originating from different production cycles within the same facility. The only compounds common to both samples were alkanes and chloroform, though the concentration of chloroform was an order of magnitude higher in sample RU07009 (1st pipe) than in sample RU07011 (2nd pipe). RU07009 additionally contained three phthalate esters (DEHP, DiBP & DEP), three fatty acids, various chlorinated solvents (dichloromethane, tetrachloromethane, tetrachloroethane, tetrachloroethene) and methylphenol. The concentration of tetrachloromethane and chloroform in this sample was at 5 and 3 times respectively the quality objective levels for the aquatic environment which was set by the EC Council Directive 86/280/EEC (EEC 1986) and amended in 1988 (EEC 1988). Chloroform is identified as a priority pollutant under the EU Water Framework Directive (EU 2000), with a proposed Annual Average Environmental Quality Standard (AA-EQS) for internal surface waters of 2.5µg/l (EC 2006). Although the concentration recorded in the wastewater at the time of sampling was substantially above this standard, it is important to note both that the standards apply to the quality of receiving waters rather than quality of discharges and that it is not possible to extrapolate from a single sample to estimate an annual average.

Sample RU07011 additionally contained a mixture of nonylphenyl (di-nonyl)phenyl amine isomers and trichloroethane. However, the later wastewater sample collected from the 2nd pipe in October 2007 (RU07039) contained, in addition to chloroform, low levels of di- and tetrachloromethanes. These contaminants had not been detected in wastewater discharged from this pipe in July, but were detected in discharges from the 1st pipe sampled at that time (RU07009). Together, these results suggest that the quality of discharges from these two pipes may vary significantly over time, perhaps depending on the precise processes being carried out within the facility at the time.

Sediment samples collected adjacent to both pipes contained polybrominated diphenyl ethers (PBDEs), chemicals which are added to a wide variety of materials, including casings and components of many electronic goods, to prevent the initiation and spread of fire. There are a total of 209 possible congeners of PBDEs, differing in the numbers of bromine atoms and their position on the diphenyl ether molecule. 14 congeners, ranging from di- to decabrominated, were detected in sample RU07010, and 6 congeners, from di- to heptabrominated, in sample RU07012. These samples also contained various PAHs and alkanes. Additionally, sample RU07010, collected close to the 1st discharge pipe of JSC “Electropult”, contained more than 60 individual congeners of the persistent organic pollutants (POPs) polychlorinated biphenyls (PCBs), ranging from mono- to hexachlorinated, with a predominance of tetra- and pentachlorinated congeners. Background information on the former uses and toxicity of PCBs is provided in Box 3.

5.1.2 Site 2 - Pirogovskaya embankment industrial zone

The single wastewater sample RU07022, collected from Site 2 - Pirogovskaya embankment industrial zone, contained a diverse range of organic compounds:

- PBDEs (5 congeners from tri- to penta-BDEs);
- substituted ketones/hydrazones, including compounds known as photoinitiators and related compounds such as derivatives of diphenylmethanone (benzophenone), diphenylethanone and dimethylanthrone;
- benzenamine (known as aniline) derivatives, including mono- and dichloro-substituted compounds;
- diethyltoluamide, widely used in insect repellent formulations;
- pyrazine derivatives, including tetramethylpyrazine which is used in the production of pharmaceuticals;
- quinoxaline derivatives, some of which are used in the chemistry of coordination polymers;
- PAHs;
- terpenoids;
- the phthalate ester diethylhexyl phthalate (DEHP);
- representatives of phenolic compounds;
- tris(monochloroisopropyl) phosphates (TMCPPs) which are used as flame retardants and known under the trade name Fyrol PCF;
- diphenylhydrazine, once used in fabric dyes but now more commonly used to make certain medicines and as a starting material in organic synthesis;
- N,N’-dimethyl-N,N’-diphenylurea, also known as Methyl Centralite, a compound that is used as a stabilizer in gun-powder and military nitrocellulose;
- Chloroform (at low concentrations).

As was mentioned earlier in this report, the wastewater outfall at the Pirogovskaya embankment industrial zone is a combined discharge of several plants of various industrial profiles and it is difficult to specify clearly which industrial sector contributes to which groups of organic contaminants in the waste stream. Nevertheless, it is worth noting that several groups of organic compounds that were detected in this sample are commonly associated with the production of electrical and electronic goods, including photoinitiators (e.g. benzophenone and acetophenone), flame retardants (PBDEs and Fyrol PCF), chemicals used in the production of insulating coatings for semiconductor devices (quinoxaline derivatives), and plasticizer (DEHP). The latter chemical, however, as well as the flame retardants, are widely used in industrial and consumer products and have become widespread environmental contaminants as a result.

Another siginficant grouping of chemicals detected in this sample are the chlorinated anilines, pyrazine derivatives, diethyltoluamide, and diphenylhydrazine, which together may indicate input from the pharmaceuticals production sector. Clearly, the presence of Methyl Centralite, a burning rate moderator and stabilizer for gun powder, in the wastewater sample RU07022 indicates input from the military goods industrial production sector.

The wastewater did not contain any of the quantified metals at levels above than their typical background concentration ranges found in uncontaminated surface waters.

Sample code	Sample type	Chloroform	Ethane, 1,1,1-trichloro-	Ethane, 1,1-dichloro-	Ethane, 1,2-dichloro-	Ethane, 1,1,2,2-tetracloro-	Ethene, tetrachloro-	Methane, bromodichloro-	Methane, dichloro-	Methane, tetrachloro-
RU07009	WW	36.6	n/d	n/d	n/d	2.1	0.4	n/d	8.6	65.2
RU07011*	WW	2.1	0.8	n/d	n/d	n/d	n/d	n/d	n/d	n/d
RU07039*	WW	4.9	n/d	n/d	n/d	n/d	n/d	n/d	1.4	1.8
RU07022	WW	2.6	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
RU07033**	WW	58.2	n/d	n/d	n/d	n/d	n/d	3.4	n/d	n/d
RU07043**	WW	77.8	n/d	n/d	n/d	n/d	n/d	4.7	n/d	n/d

*Table 7. Concentration (in μg/l) of volatile organic compounds (VOCs) in wastewater (WW) samples collected in St. Petersburg region, Russia, July and October 2007; n/d – not detected, * and ** - indicates samples collected from the same source at different time.*

5.1.3 Site 3 - JSC “Ladoga”

From site 3 – JSC “Ladoga”, two samples were collected in July 2007, a wastewater (RU07033) and a sediment (RU07034), and an additional wastewater was collected in October (sample RU07043, for VOCs analysis only). The wastewater sample collected in July contained a range of alkanes, two phthalates (DiBP and DnBP) and also chloroform at a relatively high concentration (58 μg/l). Traces of bromodichloromethane were also found. Concentrations of both chloroform and bromodichloromethane in the repeat sample collected in October (RU07043) were slightly higher, though of the same order, strongly suggesting that there is a permanent output of these VOCs via the effluents discharged from this location. In both cases, the concentration of chloroform in the wastewater exceeded the quality objective level for the aquatic environment by 5 and 6 times respectively (EEC 1986& EEC 1988). The sediment sample that was collected by the discharge outfall contained 7 PBDE congeners (from di- to pentabrominated), 1,4-dichlorobenzene, and a variety of PAHs and alkanes.

The wastewater and associated sediment did not contain any of the quantified metals at levels above what might be considered typical background concentration ranges found in uncontaminated surface water environments.

5.1.4 Site 4 - Petrogradskaya embankment industrial estate

A single sediment sample that was collected from a non-operational pipe leading from the Petrogradskaya embankment industrial estate (Site 4, sample RU07023) contained 11 PBDEs (from di- to heptabrominated), as well as PAHs, alkanes and alkenes, di- and tri-chlorobenzenes and a number of alkylbenzenes.

This sediment also contained copper and zinc at elevated concentrations, both at approximately five times levels typically found in uncontaminated freshwater sediments, and somewhat less elevated levels of cadmium and lead. Their presence suggests an impact from previous industrial discharges in the vicinity, though their exact source within the industrial zone is not known.

5.1.5 Discussion

Samples collected from four sites in the St-Petersburg area associated with electronic and electrical goods production have many similarities in the chemicals identified in waste streams and associated sediments. All sediments samples from sites 1-4 and one wastewater sample from site 2 (RU07022) contained PBDEs, a group of polybrominated chemicals widely used as flame retardants, at levels which, though not quantified, were clearly distinguishable from trace background contamination and more indicative of the presence of significant local point sources. Many PBDEs are environmentally persistent chemicals, and some are also toxic and highly bioaccumulative. More information on PDBEs is given in Box 1.

PAHs and alkanes/alkenes, which have also been identified in all sediment samples from these sites, are components of crude oil and petroleum. PAHs occur in a variety of materials such as soot, coal, tar, and tobacco smoke. They are also commonly found as products of incomplete combustion. PAHs are prevalent pollutants in both terrestrial and aquatic environments, and can cause a wide range of toxic effects (Sverdrup *et al*. 2002). Fifteen PAHs have been reasonably anticipated to be human carcinogens, based on sufficient evidence of carcinogenicity in experimental animals (DHHS 2005).

Samples from sites 1-3 contained conspicuous residues of phthalate esters, and those from sites 3 & 4 contained chlorinated benzenes. Phthalates (phthalates esters) are predominantly used as plasticizers to soften plastics (especially PVC) and have undergone large-scale and ongoing releases to the environment (CSTEE 2001). They have been detected in various environmental compartments, including in the tissues of wildlife and in the human body (Otake *et al*. 2001, Butte & Heinzow 2002, Fromme *et al*. 2004, Colon *et al*. 2000, Blount *et al*. 2000, Silva *et al*. 2004). Phthalates are relatively persistent in the environment. Among the greatest concerns relate to the toxicity of some phthalates, including DEHP and DiBP, to the developing reproductive system in mammals (Ema & Miyawaki 2002, Mylchreest *et al*. 2002). More information on phthalates is presented in Box 2.

The most diverse range of organic compounds detected in samples from this region was that identified in wastewater sample RU07022 from site 2, probably due to a number of different industrial plants discharging via the same combined outfall (see sites description).

Contamination by heavy metals was particularly marked in two locations, at sites 1 and 4, with the wastewater sample RU07011 from site 1 having the highest concentration of toxic metals such as cadmium, chromium, copper, nickel, tin and zinc recorded in this study. The exact sources of the metals present in this wastewater sample and corresponding sediment RU07012 at high concentration are not known. However, many metals have also been found at sites of wastewater discharge from electronic manufacturing facilities in other countries, particularly from facilities involved in the manufacture of printed circuit boards (Brigden *et al*. 2007). Information on the uses and toxicity of the key metals present in the discharges are given in Boxes 4-9.

Box 2. Phthalate esters

Phthalates (or, more accurately, phthalate diesters) are non-halogenated chemicals with a diversity of uses, dominated by use as plasticizers (or softeners) in plastics, especially PVC (e.g. in cables and other flexible components). Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Some phthalates are discrete chemicals, such as the well known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DINP).

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal. Within the European Union (EU) alone, this amounts to thousands of tonnes per year (CSTEE 2001). As a result, phthalates are among the most ubiquitous man-made chemicals found in the environment. They are widely found in the indoor environment, including in air and dust (Otake *et al*. 2001, Butte & Heinzow 2002, Fromme *et al*. 2004). Phthalates are commonly found in human tissues, including in blood and, as metabolites, in urine (Colon *et al*. 2000, Blount *et al*. 2000, Silva *et al*. 2004). In humans and other animals they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al*. 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is a known reproductive toxin, capable (in its monoester form MEHP) of interfering with development of the testes in early life. In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003). Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al*. 2002). Both DEHP and DBP are classified as "toxic to reproduction" within Europe. Recent research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al*. 2005). Decreased AGI correlated with concentrations of four phthalate metabolites, namely monoethyl phthalate (MEP), mono-n-butyl phthalate (MBP), monobenzyl phthalate (MBzP), and monoisobutyl phthalate (MiBP). It was also found that DBP can not only be taken up by crops and enter the food chain, but also affects proteome formation as well as the physiology and the morphology of some crops during growth (Liao 2006). Other commonly used phthalates, including the isomeric forms DINP and DIDP (diisodecyl phthalate), are of concern because of observed effects on the liver and kidney, albeit at higher doses.

At present, there are few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children's toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EC 2005). While this addresses one important exposure route, exposures through other consumer products remain unaddressed.

Box 3. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of synthetic organic chemicals that contain 209 individual compounds (known as congeners) with varying patterns of chlorine substitution. PCBs have been used in a wide variety of applications, including transformer oils, hydraulic fluids, plasticisers and carbonless copy papers. They were also used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 2000). Use in transformer oils (frequently with tri- and tetrachlorobenzenes as solvents, Swami *et al*. 1992) and capacitors accounted for the greatest tonnages (de Voogt & Brinkman 1989). Production of PCBs was banned in 1977 when their ability to accumulate in the environment and to cause harmful effects became apparent (ATSDR 2000).

PCBs enter the environment as mixtures containing a variety of individual components and impurities. At least one third of the PCBs that have been produced are now estimated to have entered the environment (Swedish EPA 1998). The other two thirds remain in old electrical equipment and in waste dumps, from which they continue to leach into the environment (for example, when obsolete equipment is dismantled, recycled and/or disposed of).

Once released to the environment from whatever source, PCBs are highly persistent. Furthermore, PCBs that are taken up by aquatic organisms and fish accumulate in them, reaching levels that may be thousands of times higher than in water (ATSDR 2000). PCBs are bioconcentrated to a factor of 6000 for fish and 47 000 for invertebrates (Jones *et al*. 1988). Train (1979) reports bioconcentration factors of between 2500 and 100 000.

PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is undoubtedly the primary route of exposure to PCBs (see e.g. review by Allsopp *et al*. 2000), although dermal exposure may be dominant amongst those directly handling PCBs or PCB-contaminated materials (Lees *et al*. 1987).

PCBs exhibit wide range of toxic effects in animals, including immunosuppression, liver damage, tumour promotion, neurotoxicity, behavioural changes and damage to both male and female reproductive systems (Seegal and Shain 1992, Safe 1993, Rice 1999). PCBs may affect not only the oestrogen system, but also the androgen system, the thyroid hormone system, the retinoid system, the corticosteroid system and several other endocrine pathways (Brouwer *et al*. 1999). Although it is difficult to assess the impact of contaminants on populations in the wild, not least because they are exposed to complex mixtures of chemical contaminants, some immunological and reproductive disorders in marine mammals have nevertheless been linked to elevated levels of persistent organochlorines, in particular the PCBs (see reviews by Allsopp *et al*. 1999, 2001a, Haave *et al*. 2003).

In humans, the greatest body of research on the toxic effects of PCBs has come from two incidents in Japan and Taiwan where people consumed cooking oil that was contaminated with PCBs and other organochlorines.. A recent review of data for children born to mothers exposed to PCBs and PCDFs in the Taiwan incident notes higher incidences of retarded growth, delayed cognitive development and behavioural problems than in children of unexposed mothers (Guo *et al*. 2004). In young men with prenatal exposure there was also significantly increased abnormal morphology of sperm. Studies on the general population of the Netherlands and the Arctic and families of Swedish fishermen (reviewed by Allsopp *et al*. 2001a, Allsopp *et al*. 1999) suggested that even relatively low levels of exposure to PCBs can result in impacts on the immune system (see also Weisglas-Kuperus *et al*. 2004) growth retardation and neurological effects.

The control of PCBs is addressed under many international legal instruments relating to environmental pollution (inter alia, the Barcelona, Helsinki, Basel, Bamako, Rotterdam, OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes). In addition, PCBs are targeted for global production ban under the 2001 Stockholm Convention on persistent organic pollutants (POPs), an instrument which also requires proper controls on destruction of stockpiles and the handling of wastes.

Box 4. Cadmium

Cadmium and its compounds are used in a number of applications within electronics products. Cadmium metal is used in some contacts, switches and solder joints. Many devices contain rechargeable nickel-cadmium (Ni-Cd) batteries which contain cadmium oxide. Cadmium compounds have also been used as stabilisers within PVC formulations, including those used as wire insulation (Matthews 1996). Cadmium sulphide has been also used in older cathode ray tubes (CRTs) as a phosphor coating, a material used on the interior surface of the screen to produce light (Li *et al*. 2004, OECD 2003).

Cadmium is a rare metal, found naturally in the environment as very low concentrations, typically below 2 mg/kg in soils and sediments (Alloway 1990, Butte & Heinzow 2002, Salomons & Forstner 1984). When released to aquatic environments cadmium is more mobile than most other metals (ATSDR 1999). Cadmium is highly toxic to plants, animals and humans, having no known biochemical or nutritional function (ATSDR 1999, WHO 1992). Exposure can result in bioaccumulation of cadmium in humans. Many animals and plants, including those consumed by humans, can also accumulate cadmium, providing an additional route of dietary exposure for humans (Elinder & Jarup 1996, Olsson *et al*. 2005).

Cadmium exposure can occur occupationally through inhalation (breathing in) of fumes or dusts containing cadmium and its compounds, or through environmental exposures, primarily diet. Cadmium is a cumulative toxicant and long-term exposure can result in damage to the kidneys and bone toxicity. For the general population and for animals, cadmium exposure through diet primarily affects the kidneys (Elinder & Jarup 1996, WHO 1992). Recent studies have demonstrated kidney damage in humans at lower levels of exposure than previously anticipated (Hellstrom *et al*. 2001). Other health effects from cadmium exposure include disruption to calcium mechanisms causing bone effects, as well as the development of hypertension (high blood pressure) and heart disease. In the short term, inhalation of cadmium oxide fumes or dusts can also affect the respiratory system (ATSDR 1999, Elinder & Jarup 1996, WHO 1992). Furthermore, cadmium and its compounds are known to be human carcinogens, primarily for lung cancer following inhalation (DHSS 2002).

There are a number of regional controls on the use of cadmium in products. EU legislation restricting the use of certain hazardous substances (ROHS) in electrical and electronic equipment prohibits the use of cadmium in new equipment put on the market from 1 July 2006 (EU 2002a), with a maximum allowable concentration of 0.01% cadmium by weight in homogeneous materials. There are exemptions to this for the use of cadmium in certain plating applications. Under legislation addressing waste electrical and electronic equipment (WEEE), batteries containing more than 0.025% cadmium by weight must be separated from wastestreams and recycled where appropriate (EU 2002b). The use of cadmium in products is further addressed under other EU legislation, including restrictions on its use as a colouring agent or stabiliser in a wide range of products (including PVC) where the cadmium content exceeds 0.01 %, with some exceptions for safety reasons (EU 1991).

5.2 Samples associated with WWTPs and landfills

The results of the analysis of 10 samples associated with WWTPs and landfills in the St-Petersburg area are presented in Tables 8 (heavy metals), 9 (organic compounds qualitative screen) and 10 (quantitative VOCs analysis). These samples included two wastewater samples from St-Petersburg's WWTPs (RU07014 - Northern WWTP and RU07015 - Central WWTP); two sediment samples, from Poligon Severny (RU07021) and the Southern municipal waste landfill (RU07025) respectively; three leachate/surface water samples from Poligon Severny (RU07020) and from Southern municipal waste landfill (RU07024 & RU07040); and two ground water samples (RU07019 and RU07041), both from Poligon Severny.

Location	**Site 5A**	**Site 5B**				**Site 6**	**Site 7**	
Sample Code	RU07014	RU07018	RU07019	RU07020	RU07021	RU07015	RU07024	RU07025
Sample type	**WW**	**Sludge**	**GW**	**Leachate**	**SED**	**WW**	**Leachate**	**SED**
	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<20	<20	<20	<20	<20	<20	<20	<20
Barium	15	266	18	20	173	43	393	113
Beryllium	<2	0.3	<2	<2	0.9	<2	<2	0.5
Bismuth	<20	<20	<20	<20	<20	<20	<20	<20
Cadmium	<5	51	<5	<5	3.9	<5	<5	3.2
Chromium	<20	65	<20	<20	68	<20	1730	50
Chromium (VI)	n/a	n/a	n/a	n/a	n/a	n/a	<200	n/a
Cobalt	<20	8	<20	<20	17	<20	38	11
Copper	<20	183	<20	<20	74	<20	380	81
Gallium	<20	<20	<20	<20	<20	<20	<20	<20
Germanium	<30	<30	<30	<30	<30	<30	<30	<30
Indium	<20	<20	<20	<20	<20	<20	<20	<20
Iron	91	n/a	3280	2230	n/a	305	6090	n/a
Lead	<50	57	<50	<50	29	<50	87	37
Manganese	91	330	205	257	777	90	872	272
Mercury	<0.5	<0.1	<0.5	<0.5	<0.1	<0.5	0.6	<0.1
Molybdenum	<20	<2	<20	<20	<2	<20	<20	<2
Nickel	<20	105	<20	<20	31	26	274	19
Selenium	<50	<30	<50	<50	<30	<50	<50	<30
Tin	<50	21	<50	<50	11	<50	731	18
Vanadium	<20	25	<20	<20	58	<20	93	33
Yttrium	<10	11	<10	<10	13	<10	<10	8
Zinc	26	856	<10	14	159	53	520	150

Table 8. Metals identified in ground water (GW), sludge, leachate, wastewater (WW) and sediment (SED) samples from WWTPs and landfills, St-Petersburg, Russia, 2007. n/a – not analysed.

5.2.1 Site 5A – Northern WWTP and site 5B - Poligon Severny

A single sample of treated wastewater (RU07014) collected from the discharge of the Northern WWTP contained remarkably few organic compounds, only two of which could be reliably identified and both of which were at trace levels (namely chloroform and 1,4-dichlorobenzene). Moreover, concentrations of metals in this wastewater were all within the ranges typically seen in uncontaminated surface waters.

However, a sample of sludge (RU07018) collected from a slime pit from Poligon Severny, where sludges generated by Northern WWTP are disposed of, contained a range of various classes of organic compounds, including PBDEs (23 congeners from di- to deca-BDE), chlorinated benzene and chlorinated aniline, numerous PAHs, alkylbenzenes, butylated hydroxytoluene (BHT), cyclic siloxanes and many alkanes and alkenes. In total, 188 individual organic compounds were resolved from this sample, though fewer than half could be identified to any degree of reliability. The presence of PBDEs, both lower and higher bromo-substituted congeners, may demonstrate input from various waste streams that contained different technical mixtures of PBDEs (penta-, octa- or deca-BDE). Another factor that might be important is debromination of the higher-substituted congeners, resulting in increasing concentrations of lower-substituted PBDEs over time. The sludge also contained a high concentration of cadmium, a highly toxic metal usually found only at very low levels in the environment, as well as other metals at somewhat elevated concentrations (including copper and zinc and, to a lesser extent, lead and nickel).

The presence of these metals and certain organic chemicals in the sludge demonstrates their input to the WWTP from untreated effluent. While some organic chemicals are destroyed during wastewater treatment, much of the heavy metals and some of the most persistent and toxic organic chemicals are generally only scavenged from wastewaters into the sludge during treatment. This is consistent with the low levels of metals seen in the discharged wastewater sample. As a result, WWTPs simply concentrate heavy metals and certain persistent organic contaminants in solid residues which, far from providing a solution, is merely the transfer of contamination from one environmental medium to another, creating an additional contaminated wastestream that must be dealt with.

A similar range of organic compounds was detected in the sediment sample RU07021, collected from a drainage canal next to the hill where the slime pit is located. Furthermore, the latter sample also contained 15 PCBs congeners (from di- to hexachlorinated with domination of pentachlorinated congeners), as well as cadmium, copper and zinc at levels somewhat elevated above average background concentrations in soils and sediments, indicating the movement, possibly by leaching, of metals from the sludge disposal areas. These metals tend to be more mobile than other metals present in the sludge sample (Salomons & Forstner 1984). It should be noted that, while the sample of leachate/surface water RU07020 from this drainage canal did not contain elevated levels of metals, nor PBDEs, this is likely because such contaminants bind preferentially to sedimentary inorganic or organic particles. Organic compounds detected in this sample included 1,4-dichlorobenzene at trace levels, two phthalates (DiBP & DnBP), alkanes, silicone oil derivatives and 3-hexenedinitrile, also known as 1,4-dicyano-2-butene. Nitrile compounds are synthesized on a large scale as solvents, plastics intermediates, synthetic rubber chemicals, pharmaceuticals, herbicides and as starting materials for other chemicals. However, they are notoriously poisonous.

Box 5. Copper

Copper is widely used within electronics products due to its high electrical conductivity, primarily as a pure metal, or as part of mixtures (alloys) with other metals (ATSDR 2004, OECD 2003). Levels of copper in the environment are typically quite low, with soils containing less than 30 mg/kg, and only slightly higher levels (less than 50 mg/kg) in freshwater sediments (Alloway 1990, ATSDR 2004, Salomons & Forstner 1984). Background concentration of soluble copper in uncontaminated surface waters can vary significantly, but average levels are typically below 10 µg/l (ATSDR 2004, Salomons & Forstner 1984).

Copper is an important element for humans and animals in low doses, though expose to high levels of bioavailable copper can lead to bioaccumulation and toxic effects (ATSDR 2004). However, many aquatic organisms are extremely sensitive to copper, particularly in soluble forms, and releases of soluble copper compounds to aquatic environments can have significant impacts. Copper in soluble forms is highly mobile in the aquatic environment, particularly at higher acidity. In these forms, copper is far more bioavailable and is toxic to a wide range of aquatic plants and animals (ATSDR 2004, Gerhardt 1993). Effects can occur at very low levels, including reductions in growth and fertility rates as well as increased mortality (Bryan & Langston 1992). Although dependent of many others factors, the majority of aquatic organisms cannot tolerate or survive at copper concentrations above 1 mg/l (1000 µg/l), and impacts can occur at concentrations as low as 0.05 mg/l (50 µg/l) for some sensitive organisms (Nor 1987, Salomons & Forstner 1984). The World Health Organisation (WHO) set a drinking water guideline value for copper of 2000 µg/l (WHO 2006).

Location	**Site 5A**	**Site 5B**				**Site 6**	**Site 7**	
Sample Code	RU07014	RU07018	RU07019	RU07020	RU07021	RU07015	RU07024	RU07025
Sample type	**WW**	**Sludge**	**GW**	**Leachate**	**SED**	**WW**	**Leachate**	**SED**
No. of organic compounds isolated	6	188	139	80	108	52	158	143
No. of reliably identified compounds (% of total)	2(33%)	92(49%)	22(16%)	20(25%)	47(44%)	18(35%)	46(29)	58(41)
Halogenated VOCs	(1)	n/a	-	-	n/a	(2)	-	n/a
PBDEs	-	(23)	-	-	(9)	-	(8)	(13)
PCBs	-	-	-	-	(15)	-	-	(12)
Chlorinated benzenes	(1)	1	-	(1)	(1)	-	(1)	1(1)
Chlorinated anilines	-	1	-	-	-	-	-	-
Phthalate esters	-	-	1	2	-	1	-	-
DDT metabolites	-	-	-	-	-	-	-	(1)
PAHs	-	19	1		13		3	4
Alkyl benzenes	-	4	-	-	-	-	1	-
Nitrile compounds	-	-	1	1	-	-	-	-
Substituted phenols	-	1				1		-
Silicone containing compounds	-	1	1	1	-	-	-	-
Sulphur or sulphur containing compounds	-	-	-	-	-	1	-	1
Alkanes & alkenes	-	32	16	15	14	13	-	23
Other hydrocarbons	-	10	2	-	-	-	3	2

Table 9. Organic chemicals identified in ground water (GW), sludge, leachate, wastewater (WW) and sediment (SED) samples from WWTPs and landfills, St-Petersburg, Russia, 2007. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; n/a – not analysed; (-) – not detected.

The sample of ground water RU07019 collected from a borehole on Poligon Severny contained a similar range of compounds to those detected in the drainage canal surface water sample RU07020, including DiBP and 3-hexenedinitrile. However, this ground water did not contain any of the quantified metals at elevated levels other than iron. No VOCs were detected in either ground water sample RU07019 and RU07041.

Box 6. Zinc

Zinc has a variety of uses in electrical products; in batteries, as a protective coating for other metals, and zinc compounds have been used as stabilisers in PVC formulations (ATSDR 2005c, Matthews 1996). Levels of zinc are generally quite low in the environment; in uncontaminated soils and sediments levels are typically below 100 mg/kg, while in uncontaminated fresh surface waters and groundwater levels are typically below 50 µg/l (ATSDR 2005c, Salomons & Forstner 1984).

Zinc is an essential nutrient for humans and animals, though exposure to high concentrations of bioavailable zinc can result in significant bioaccumulation with possible toxic effects (ATSDR 2005c). High doses of zinc in humans can induce a range of symptoms, including pancreatic damage, anaemia, gastrointestinal distress and diarrhoea. Similar effects are also seen in animals (ATSDR 2005c, Goyer 1996). The World Health Organisation does not set a drinking water guideline value for zinc, but levels up to 3 mg/l (3000 µg/l) are not considered unacceptable (WHO 2006).

Sample code	Sample type	Chloroform	Ethane, 1,1,1-trichloro-	Ethane, 1,1-dichloro-	Ethane, 1,2-dichloro-	Ethane, 1,1,2,2-tetracloro-	Ethene, tetrachloro-	Methane, bromodichloro-	Methane, dichloro-	Methane, tetrachloro-
RU07014	WW	1.2	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
RU07015	WW	0.8	n/d	n/d	1.4	n/d	n/d	n/d	n/d	n/d
RU07019	GW	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
RU07040	L	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
RU07041	GW	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d

Table 10. Concentration (in µg/l) of volatile organic compounds (VOCs) in wastewater (WW), groundwater (GW) and leachate (L) samples collected in St. Petersburg region, Russia, July and October 2007; n/d – not detected.

Thus, the range of compounds identified in the samples collected from Poligon Severny which receives sludges from North WWTP, indicates that this treatment plant receives wastewaters that contain wide range of environmental pollutants accumulated in sludges (e.g. PBDEs and heavy metals). These can, in some cases, cause secondary contamination when disposed on the landfills.

5.2.2 Site 6 - Central WWTP

A single wastewater sample (RU07015) from Central WWTP was collected from an underwater dispersing head which spreads treated wastewater into Nevskaya Guba. A larger number of individual organic compounds was isolated from this sample than from the wastewater sample (RU07014) collected from the discharge of the Northern WWTP. Compounds identified in effluent from the Central WWTP included the phthalate DnBP, a benzothiazole derivative, tert-butylphenol (an alkylphenol, and possible degradation product of surfactants such as alkylphenol polyethoxylates (APEOs)), alkanes, chloroform and 1,2-dichloroethane, albeit at low part per billion (µg/l) levels. In contrast, this wastewater did not contain any of the quantified metals above levels typically seen in uncontaminated surface waters.

The detection of a wide variety of compounds in this sample, including the chlorinated solvent 1,2-dichloroethane, despite the fact that sample was taken underwater (with significant dilution of raw effluent by the receiving water therefore expected), indicates that the treatment of this wastewater is limited in its effect.

5.2.3 Site 7 - South Municipal Waste Landfill

PBDEs were readily identified in both samples collected from swamp area located on the territory of the South Municipal Waste Landfill, between the old and current part of the landfill (leachate/surface water RU07024 and sediment RU07025), with 9 congeners in the leachate sample (from tri- to heptabrominated) and 13 congeners in the sediment sample (from di- to heptabrominated). As was mentioned above, this landfill receives all types of domestic wastes, including obsolete electrical and electronic equipment which is generally considered a key source of materials containing PBDEs. Both samples also contained PAHs, chlorinated benzenes (1,4-dichlorobenzene in both samples and 1,2,4-trichlorobenzene in the sediment only) and range of alkanes and alkenes. Additionally, the sediment sample contained 12 PCB congeners (from tri- to hexachlorinated), and trace levels of the pesticide residue p,p'-DDE.

Leachate/surface water sample RU07040 was collected in October 2007 from the same place as sample RU07024, but subject to VOCs analysis only. No VOCs were detected in this sample. It is not known whether this second sample was otherwise chemically similar to RU07024, collected from the same location in July 2007.

The leachate also contained metals at concentrations higher than usually present in surface waters including copper, lead, mercury and zinc. This sample also contained high levels of iron, tin and chromium (though not the most toxic form, hexavalent chromium (VI), in which soluble chromium is usually present). The leachate sample was dark and turbid, suggesting high levels of organic matter which can help solubilise these metals (which are not generally present in waters at such high levels) and generally increase the mobility of all metals.

These data indicate movement of organic compounds and heavy metals from wastes disposed of at this site. However, high metal levels were not found in the sediment from this site other than moderately elevated levels of cadmium, copper and zinc, all at similar levels to those in the sediment from the leachate channel at the sewage sludge landfill, site 5B (RU07021)

5.3 Samples associated with e-wastes open burning sites

The results of analyses for four samples of ash-contaminated soil (RU07035-RU07038) that were collected from three locations around St-Petersburg city where open air burning of electronic wastes is taking place are presented in Tables 11 and 12.

All four of these samples contained high concentrations of many metals, all with known uses in electrical and electronic equipment and therefore commonly present in waste electrical and electronic equipment. For example, lead has been widely used in electrical solder (Geibig & Socolof 2005), and cadmium in contacts, switches and certain rechargeable batteries. Compounds of lead, cadmium, zinc and barium have all been used and as stabilisers in PVC, a plastic widely used as coating on wires and cables (Matthews 1996), while antimony compounds are used in flame retardant formulations (Lau *et al*. 2003). For additional information on their uses and toxic properties see Boxes 4-9.

Box 7. Lead

Lead has many uses in electronics products. Metallic lead is used in electrical solder, primarily on printed circuit boards (commonly as an alloy with tin). Lead oxide is used in the glass of cathode ray tubes (CRTs), which contain approximately 2-3kg of lead in older models and 1 kg in newer models (OECD 2003). In addition, lead compounds have been used as stabilisers in PVC formulations (Matthews 1996).

Concentrations of lead in the environment are generally low. Soils and freshwater sediments typically contain less than 30 mg/kg (Alloway 1990, Butte & Heinzow 2002, Salomons & Forstner 1984). Under landfill conditions lead can leach from CRT glass (Musson *et al*. 2000). Incineration can also result in release of lead to the air as in the ash produced (Allsopp *et al*. 2001). Releases of lead oxide dust or lead fumes may also occur during glass crushing or high temperature processing, including smelting (OECD 2003). Following release to the environment lead has low mobility compared to most metals.

Workers involved in high temperature processes, such as at lead smelters, can be significantly exposed to lead fumes (Schutz *et al*. 2005). Workers using lead based solders may also be exposed to lead-bearing dusts and fumes (ATSDR 2007b). Following exposure humans can accumulate lead, as can many plants and animals (Sauve *et al*. 1997, ATSDR 2007b). Where soils and dusts are contaminated with lead, children can be particularly exposed through hand-to-mouth transfer (Malcoe *et al*. 2002). Children living in an area in China where electronic wastes are recycled and disposed of have been found to have elevated blood lead levels (Huo *et al*. 2007)

Lead is highly toxic to humans as well as many animals and plants. Lead exposure is cumulative; the effects of exposure are the same whether through ingestion or inhalation, and some appear to be irreversible (ATSDR 2007b, Bellinger & Dietrich 1994, Goyer 1996). In humans, lead has a wide range of effects including damage to the nervous system and blood system, impacts on the kidneys and on reproduction. Of particular concern is the effect of low-level exposure on brain development in children, which can result in intellectual impairment (Canfield *et al*. 2003). Similar toxic effects are seen in animals, and lead is also toxic to all aquatic life (WHO 1989, Sadiq 1992).

A number of regional controls exist on the use of lead in products. EU legislation restricting the use of certain hazardous substances (ROHS) in electrical and electronic equipment, prohibits the use of lead in new equipment put on the market from 1 July 2006 (EU 2002a), with a maximum allowable concentration of 0.1% lead by weight in homogeneous materials, with certain exemptions. EU legislation addressing waste electrical and electronic equipment (WEEE) specifies that batteries containing more than 0.4% lead by weight must be separated from wastestreams and recycled where appropriate (EU 2002b). In addition, the European PVC industry has a voluntary agreement to phase out lead stabilisers in PVC by 2015 (ENDS 2002).

For the metals antimony, copper, lead and zinc, the concentrations where of a similar order of magnitude across all four samples. In the case of cadmium, however, one sample (RU07038, from site 10) contained a far higher concentration (250mg/kg) than that found in the other sample from site 10, and those recorded in both samples from the other two sites (14-33 mg/kg). In all cases, the concentrations of all these metals in the four samples far exceeded those typically seen in uncontaminated soils, ranging from tens to hundreds of times above typical background levels (Alloway 1990, Salomons & Forstner 1984). In addition, the samples from sites 8 and 9 (RU07035 and RU07036 respectively) also contained high concentrations of barium and tin, not seen in the two samples from site 10. Overall, the elevated concentration ranges of metals in these samples were similar to those previously reported for samples collected from electronic waste burning sites in China and India, although both antimony and tin were generally found at far higher levels in that previous study (Brigden *et al*. 2005).

Box 8. Antimony

Antimony is a naturally occurring element with a number of industrial uses. For example, antimony compounds are used in semiconductors (antimony trihydride or stibine, Sb2H3) and as a flame retardant in plastics and other polymers (antimony trioxide, Sb2O3, Jenkins *et al*. 2000, Lau *et al*.2003), normally in combination with brominated flame retardants, especially PBDEs. Antimony is also used in the manufacture of lead acid starter batteries (both Sb2H3 and Sb2O3, Kentner *et al*. 1995) and occurs as a component of electrical solders. Although occurring naturally in soils and sediments, concentrations are commonly rather low.

Antimony shows many chemical similarities to arsenic (Andrewes *et al*. 2004). Like arsenic, it can undergo methylation as a result of microbiological activity (i.e. to form its trimethyl derivative, often called trimethylstibine), albeit at slower rates than for arsenic (Jenkins *et al*. 2000, Patterson *et al*. 2003). It also shows some similarities in its toxic effects, especially to skin cells (Patterson *et al*. 2003). However, unlike arsenic, there are relatively few studies concerning the toxicity and ecotoxicity of antimony and its compounds.

Those studies which are available indicate that the toxicity of antimony depends greatly on its particular form (i.e. its oxidation state). Trivalent antimony, such as is present in antimony trihydride and antimony trioxide, is the most toxic state whereas its pentavalent form is far less toxic (Flynn *et al*. 2003, Patterson *et al*. 2003). Some organic antimony compounds (including trimethylstibine) are very toxic (Andrewes *et al*. 2004). Antimony compounds have been associated with dermatitis and irritation of respiratory tract, as well as interfering with normal function of the immune system (Kim *et al*. 1999).

Antimony trioxide is listed by the International Agency for Research on Cancer (IARC) as “possibly carcinogenic to humans”, with inhalation of dusts and vapours the critical route of exposure. Although this compound can be lost in vapour form from items such as PVC mattress covers during normal use (Jenkins *et al*. 2000), it is in occupational settings in which the greatest exposures and concerns arise. For example, several workers exposed to high levels of antimony dust and antimony trioxide fumes at a metal brazing plant developed severe skin problems, even at levels previously thought to be safe (White *et al*. 1993).

Metabolism of antimony compounds in humans is similarly poorly studied. There is some evidence that inorganic antimony compounds, if ingested, can be converted to organic compounds and reduced to the more toxic trivalent forms in the body (Andrewes *et al*. 2004). Antimony compounds can be detected in human urine samples from both occupationally and non-occupationally exposed individuals, with levels in blood and urine correlating with levels in workplace air for those occupationally exposed (Kentner *et al*. 1995, Krachler and Emons 2001).

All the metals present at high levels at all four sites are noted for their toxicity. Of particular concern are the high levels of lead and cadmium, both of which are highly toxic and can build up in the body following repeated exposures. For barium and inorganic tin, found in high levels at sites 8 and 9, exposure does not usually cause toxic effects in humans or animals, unless ingested in very large amounts (ATSDR 2005a, ATSDR 2007a). Nonetheless, their presence at two sites in high concentrations provides further evidence of the release of such chemicals from the uncontrolled open-burning of waste electrical and electronic equipment.

These samples also contained several classes of organic pollutants that can be associated with e-wastes, including the flame retardant PBDEs and a variety of chlorinated benzenes (detected in all four samples). In addition, residues of PCBs were detected in sample RU07035. Despite the fact that PCBs have been banned for a length of the time due to their toxic properties, these chemicals are still frequently found in environmental compartments as they have been produced in vast amounts in the past and had a variety of uses. However, their detection in the screening method applied in this study indicates a presence well above trace levels, probably indicative of a specific waste-related source. The presence of chlorinated benzenes, which can be formed during burning of PVC (Ruokojarvi *et al*. 2000), might indicate that the composition of the sample included such plastics. However, other possible sources cannot be ruled out. A similar range of organic contaminants has been detected in soils from China in areas with e-wastes burning activities (Brigden *et al* 2005).

Other compounds detected in these soils included a range of akylbenzenes that were very abundant in all samples, PAHs, numerous alkanes/alkenes and, in sample RU07037 only, what appear to be short chain chlorinated alkanes or paraffins (SCCPs). SCCPs have been widely used as extreme pressure lubricants in the metal processing industry, but have also been used as flame retardants or other additives in rubbers, paints and sealants and as finishing agents for leather goods and certain textiles (OSPAR 2001). To some extent, SCCPs were used as replacements for PCBs (polychlorinated biphenyls) when these were phased out. SCCPs are very toxic to aquatic organisms and have been classified as "Category 3" carcinogens. Uses of SCCPs are now restricted within Europe and these compounds are proposed for inclusion in the Stockholm Convention on Persistent Organic Pollutants (POPs). Further background information on SCCPs is provided in Box 10.

It is necessary to mention that the pattern of PBDEs congeners detected differed significantly between these four samples. Samples RU07035 (from site 8) and sample RU07037 (from site 10) contained 25 and 19 congeners respectively, ranging from di- to deca-brominated forms. Sample RU07038 (from site 10) contained only 11 congeners, and of middle range PBDEs from tri- to hepta-BDE, while sample RU07036 (from site 9) showed the presence of only 4 congeners, deca-BDE and three nona-BDE congeners. These differences in patterns may well reflect differences in the types of equipment and materials that were burnt on the different sites. It is known, for example, that commercial penta-BDE (a mixture of lower-brominated congeners) was used predominantly for flame retardant purposes as an additive in consumer products manufactured by the furniture industry. Commercial octa-BDE, also a mixture of congeners, has been used by the plastics industry almost exclusively to flame retard acrylonitrile-butadiene-styrene (ABS) terpolymers used in computer casings and monitors. The commercial deca-BDE, which in contrast is a relatively pure formulation, is used in a variety of polymer applications, predominantly in high impact polystyrene (HIPS), such as that used in the television industry for cabinet backs, as well as for a large number of other polymers with end-uses in electrical and electronic equipment (e.g., computers, connectors, electrical boxes, wire and cable, etc.). The PBDE congeners found on site 9 (sample RU07036) were typical representatives of deca-BDE technical mixture, with the deca-BDE congener itself (BDE-209) being the most abundant.

Location	**Site 8**	**Site 9**	**Site 10**	
Sample Code	RU07035	RU07036	RU07037	RU07038
Sample type	**Soil**	**Soil**	**Soil**	**Soil**
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Antimony	189	295	303	414
Arsenic	<20	<20	<20	<20
Barium	1700	2650	111	267
Beryllium	<0.2	0.6	<0.2	<0.2
Bismuth	<20	<20	<20	<20
Cadmium	24	33	14	250
Chromium	50	81	19	18
Cobalt	16	17	17	5
Copper	8120	5350	2400	5250
Gallium	<20	<20	<20	<20
Germanium	<30	<30	<30	<30
Indium	<20	<20	<20	<20
Lead	4600	3825	3930	5630
Manganese	339	650	287	330
Mercury	<0.2	<0.2	<0.2	<0.2
Molybdenum	<2	4	<2	<2
Nickel	33	28	19	14
Selenium	<30	<30	<30	141
Tin	120	184	14	<10
Vanadium	21	29	11	18
Yttrium	5	4	4	5
Zinc	4310	14700	9020	6430

Table 11. Metals identified in soil samples from electronic wastes open burning sites, St-Petersburg, Russia, 2007.

Location	**Site 8**	**Site 9**	**Site 10**	
Sample Code	RU07035	RU07036	RU07037	RU07038
Sample type	**Soil**	**Soil**	**Soil**	**Soil**
No. of organic compounds isolated	213	264	298	191
No. of reliably identified compounds (% of total)	114(54%)	53(20%)	81(27%)	74(39%)
PBDEs	(25)	(4)	(19)	(11)
PCBs	(17)	-	-	-
Chlorinated benzenes	6(2)	3(4)	1(6)	1(7)
Short chain chlorinated alkanes	-	-	3	-
Terphenyls	5	-	-	5
PAHs	11	3	3	-
Alkyl benzenes	13	13	14	14
Alkanes and alkenes	31	24	30	23
Other hydrocarbons	4	-	5	6

Table 12. Organic chemicals identified in soil samples from electronic wastes open burning sites, St-Petersburg, Russia, 2007. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; n/a – not analysed; (-) – not detected.

The situation in which electrical and electronic wastes are being burnt in an uncontrolled and unregulated manner is of substantial concern, not least because it is likely to lead to significant contamination of the surrounding environment with toxic metals and persistent organic chemicals (through, e.g. leaching and run-off, wind-blown dusts, etc.) and result in both direct and indirect human exposure to high levels of such contaminants. It is unknown how many such places there are around the St-Petersburg area. Clearly this is an issue which requires urgent investigation and effective intervention by the local authorities.

5.4 Environmental samples

Nearly every year, the Neva River rises and St-Petersburg suffers flooding, usually at the end of autumn. This event is the result of a combination of climatic factors, including low-pressure air movement from the West, which in turn creates so-called 'long waves' which bring additional water into the Gulf of Finland and the mouth of the Neva River. Strong westerly winds then effectively block the flow of water from the Neva into the Gulf of Finland, and the river level is forced to rise, often by several meters. This may, in turn, cause superficial layers of sediments to move upstream from the lower part of the river towards the upper reaches. It is, therefore, difficult to trace point source contamination based on sediment samples analysis alone. Nevertheless, the data on river sediment samples analysis presented in this study are the first attempt to evaluate in broader terms levels of contamination of the Neva River in the St-Petersburg area, and the possible contribution to these from the electrical and electronic goods production sector. The results of organic analysis and heavy metals in the water and sediment samples from the Neva River are presented in Tables 13-16.

St-Petersburg's local environmental authority performs water monitoring in the Neva River on a regular basis and publishes the results annually. The parameters monitored included general physico-chemical characteristics, along with quantitative determination of petroleum products, phenols, synthetic surfactants, and several metals (iron, aluminium, copper, lead, zinc and manganese, CNREP 2006). However, sediment samples from the Neva River are not monitored at all by the governmental authority, and the presence of numerous other metals and organic compounds of toxicological significance (as discussed above) may go entirely unrecorded.

The current study has shown that contamination of sediments from the Neva River in the vicinity of specific industrial discharges is of concern, as all such samples contained PBDEs (up to 15 congeners in sample RU07006) and PAHs (up to 44 compounds of this class in sample RU070030). In addition, some contained other persistent pollutants, such as chlorinated benzenes (all but one sample, RU07008, contained from 1 to 5 different forms) and PCBs (24 congeners were detected in sample RU07008).

Box 10. Short-Chain Chlorinated Paraffins (SCCPs)

Chlorinated paraffins are organochlorine chemicals simply produced by reacting chlorine gas with paraffins (hydrocarbons). Short-chain chlorinated paraffins, or SCCPs, are those which have a carbon backbone of between 10 and 13 carbon atoms (C10-C13).

SCCPs have been used in a wide range of industrial and consumer applications, including use as components of industrial cutting oils for metal working, as flame retardants or other additives in rubbers, paints and sealants and as finishing agents for leather goods and certain textiles (OSPAR 2001). To some extent, SCCPs were used as replacements for PCBs (polychlorinated biphenyls) when these were phased out.

SCCPs are persistent organic pollutants with a high potential to accumulate in biological tissues. Because of the way in which they are produced, SCCPs are complex mixtures of individual chemicals, varying in chain length and degree of chlorination. This makes their study very difficult, such that data on distribution and effects still remain limited.

Nevertheless, SCCPs have been detected in a range of freshwater (mussels, fish), marine (fish, seals, whales) and terrestrial (rabbits, moose, osprey) organisms and in humans (Stern and Tomy 2000). As a result of their persistence and ability to be carried on air -currents, they are now widespread environmental contaminants, even appearing in remote areas of the Arctic (Tomy *et al*. 1999). Recent research has found that SCCPs are also widespread contaminants in the air in the UK (Peters *et al*. 2000), despite earlier assumptions used in risk assessments that any concentrations in the atmosphere would be “very small”. No published levels could be found for household dusts.

SCCPs are very toxic to fish and other aquatic organisms, and have been shown to cause damage to the liver, kidney and thyroid in rats following long-term exposure in the laboratory (Farrar 2000). Information on impacts of long-term low level exposure remains very limited (Fisk *et al*. 1999). Because of the known hazards, however, SCCPs have been classified as “Category 3” carcinogens (“possible risk of irreversible effects”) and as “Dangerous for the Environment” (“very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment”) under the EC’s Classification and Labelling Directive. The primary exposure route for humans is likely to be through food, although the significance of other routes (including contact with products, inhalation in the indoor environment and contact with contaminated dusts) has never been properly evaluated.

Because of the hazards they pose to the marine and freshwater environment, SCCPs have long been recognised as priorities for regulatory action. In 1998, the Ministerial Meeting of OSPAR agreed on the target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment by 2020 (the “one generation” cessation target) and included SCCPs on the first list of chemicals for priority action towards this target (OSPAR 1998). More recently, SCCPs have been included on the list of “priority hazardous substances” under the Water Framework Directive, such that action to prevent releases to water within 20 years will be required throughout Europe (EU 2001).

In terms of more specific measures, the Paris Commission (now part of the OSPAR Commission) agreed in 1995 on a prohibition of the use of SCCPs in a wide range of uses within the North-East Atlantic region (PARCOM 1995), including in metal working fluids, as additives in paints and sealants and as flame retardants in rubbers and plastics. This decision still remains to be fully implemented.

In the mean time, the EU has completed a risk assessment for SCCPs (EC 2000) and agreed upon restrictions only for use in metal working and leather processing (EU 2002). This leaves almost half of current uses within the EU, mainly uses in consumer products, unregulated. Inevitably, the risk assessment was based on very limited data in some areas, especially regarding toxicity to sediment and soil-dwelling animals and to humans.

During 2003, the EU will consider extending the prohibition on marketing and use to cover these other uses. So far, however, its Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 2002) has advised against further controls, despite the hazards which SCCPs present and despite the CSTEE’s recognition that some uses of SCCPs could continue to increase and that imports as components of products could be high. It is clear that current EU restrictions will not only fail to ensure that OSPAR’s cessation target for SCCPs will be met in full, but will also permit continued exposure to, and environmental releases of, SCCPs from a diversity of products containing them.

Sampling from effluent pipe located in front of JSC "Ladoga", discharging into the Neva River, St-Petersburg, Russia, 2007. © Greenpeace

The presence of PBDEs in all sediment samples starting from the very beginning of the Neva River down to its delta in the Nevskaya Guba, part of the Gulf of Finland, may indicate long term discharge of these chemicals into the river and, possibly, even into the Ladoga Lake from which Neva River originates. PBDEs are persistent and highly bioaccumulative chemicals which have been found in sediments, fish, bird eggs, and humans (Allchin & Morris 2002, Asplund *et al*. 1999 a& b, Hites 2004, Lindstrom *et al*. 1997, Meneses *et al*. 1999, Strandman *et al*. 1999, She *et al*. 2000). Further background information on PBDEs is provided in Box 1. The discharges of wastewaters from the electronics sector manufacture are possible sources of contamination of river sediments by these persistent organic compounds, as a number of industrial sites involved in electronics production are known to discharge wastewaters directly into the Neva River.

Contamination of the Neva River sediments by a diverse range of PAHs and aliphatic hydrocarbons undoubtedly results in part from spillage of fuel and lubrication oil from the engines of the numerous boats and ships operating along the Neva River, as well as from formation of PAHs as a result of incomplete combustion, though other more specific industrial sources cannot be ruled out.

Several representatives of PAHs that were detected in this study in the Neva River sediments have been reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity in experimental animals (DHHS 2005), they are: Benz[a]anthracene and Benzo[a]pyrene – detected in four sediment samples; Benzo[b]fluoranthene – detected in three sediment samples; Benzo[k]fluoranthene, Indeno[1,2,3-cd]pyrene and 5-methylchrysene – detected in one sample. However, sediments from the upper part of the river (site 11) contained in general lower numbers of aliphatic hydrocarbons and PAHs than samples from middle and lower parts of the river. PAHs are toxic compounds to both aquatic organisms and humans. Further background information on PAHs is provided in Box 11.

Chlorinated benzenes have been detected in Neva River sediment samples from all sites 11-16. These compounds have been used in a variety of applications, including as solvents, fungicides, intermediates in the manufacture of antioxidants, dyes, pigments, pharmaceuticals, and agricultural chemicals, and can also be formed unintentionaly as by-products of industrial chlorine chemistry. It is difficult to say at this stage what could be the main source of chlorinated benzenes in the Neva River; further investigations would be required in order to determine likely sources. These chemicals are persistent, bioaccumulative and have wide range of toxic effects on aquatic organisms and mammals. Further background information on chlorinated benzenes is provided in Box 12.

Location	**Site 11**			**Site 12**		**Site 13**	
Sample Code	RU07026	RU07027	RU07028	RU07031	RU07032	RU07029	RU07030
Sample type	**RW**	**SED**	**SED**	**SED**	**RW**	**RW**	**SED**
	(µg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20
Arsenic	<20	<20	<20	<20	<20	<20	<20
Barium	21	23	29	83	22	24	146
Beryllium	<2	<0.2	<0.2	<0.2	<2	<2	0.5
Bismuth	<20	<20	<20	<20	<20	<20	<20
Cadmium	<5	<0.5	<0.5	<0.5	<5	<5	<0.5
Chromium	<20	7	7	8	<20	<20	28
Cobalt	<20	2	3	4	<20	<20	11
Copper	<20	3	5	8	<20	<20	46
Gallium	<20	<20	<20	<20	<20	<20	<20
Germanium	<30	<30	<30	<30	<30	<30	<30
Indium	<20	<20	<20	<20	<20	<20	<20
Iron	92	n/a	n/a	n/a	69	55	n/a
Lead	<50	7	6	10	<50	<50	98
Manganese	<10	117	151	175	<10	<10	583
Mercury	<0.5	<0.1	<0.1	<0.1	<0.5	<0.5	<0.1
Molybdenum	<20	<2	<2	<2	<20	<20	<2
Nickel	<20	5	3	5	<20	<20	18
Selenium	<50	<30	<30	<30	<50	<50	<30
Tin	<50	<10	<10	<10	<50	<50	<10
Vanadium	<20	8	9	11	<20	<20	29
Yttrium	<10	4	5	6	<10	<10	12
Zinc	10	22	17	49	<10	<10	246

Table 13. Metals identified in river water (RW) and sediments (SED) from Neva River, St-Petersburg, Russia, 2007. n/a – not analysed;

Location	**Site 11**			**Site 12**		**Site 13**	
Sample Code	RU07026	RU07027	RU07028	RU07031	RU07032	RU07029	RU07030
Sample type	**RW**	**SED**	**SED**	**SED**	**RW**	**RW**	**SED**
No. of organic compounds isolated	127	25	38	209	24	96	168
No. of reliably identified compounds (% of total)	17(13%)	18(72%)	18(47%)	56(27%)	1(4%)	18(19%)	64(50%)
PBDEs	-	(10)	(7)	(10	-	-	(6)
Chlorinated benzenes	-	(1)	(1)	(1)	-	-	(3)
Phthalate esters	1	-	-	-	1	-	-
PAHs	-	1	1	28	-	-	44
Benzo[b]thiophene & derivatives	-	-	-	8	-	-	4
Alkanes and alkenes	16	5	8	6	-	18	20
Other hydrocarbons	-	1	1	3	-	-	7

Table 14. Organic chemicals identified in river water (RW) and sediments (SED) from Neva River, St-Petersburg, Russia, 2007. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; n/a – not analysed; (-) – not detected.

Location	**Site 14**				**Site 15**				**Site 16**	
Sample Code	RU07001	RU07002	RU07003	RU07004	RU07005	RU07006	RU07007	RU07008	RU07016	RU07017
Sample type	**RW**	**SED**	**SED**	**SED**	**RW**	**SED**	**SED**	**SED**	**RW**	**SED**
	(µg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(µg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(µg/l)	(mg/kg)
Antimony	<20	141	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<20	287	<20	<20	<20	<20	<20	<20	<20	<20
Barium	60	747	105	274	25	41	93	201	30	48
Beryllium	<2	1.8	<0.2	0.4	<2	<0.2	<0.2	0.4	<2	0.5
Bismuth	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Cadmium	<5	8.0	<0.5	1.2	<5	<0.5	<0.5	0.7	<5	<0.5
Chromium	<20	161	19	33	<20	8	27	30	<20	13
Cobalt	<20	61	4	9	<20	3	5	8	<20	6
Copper	<20	2160	107	91	<20	20	87	70	<20	13
Gallium	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Germanium	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Indium	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Iron	1410	n/a	n/a	n/a	58	n/a	n/a	n/a	1260	n/a
Lead	<50	607	35	38	<50	17	38	36	<50	17
Manganese	273	302	104	309	<10	96	131	215	29	672
Mercury	<0.5	0.3	0.2	<0.1	<0.5	<0.1	<0.1	1.1	<0.5	<0.1
Molybdenum	<20	50	<2	2	<20	<2	<2	<2	<20	<2
Nickel	<20	33	8	21	<20	10	9	16	<20	8
Selenium	<50	<30	<30	<30	<50	<30	<30	<30	<50	<30
Tin	<50	18	<10	<10	<50	<10	<10	<10	<50	<10
Vanadium	<20	29	10	24	<20	8	15	31	<20	16
Yttrium	<10	4	5	7	<10	5	6	9	<10	8
Zinc	17	11400	262	314	12	85	246	312	11	36

Table 15. Metals identified in river water (RW) and sediments (SED) from Neva River, St-Petersburg, Russia, 2007. n/a – not analysed;

Location	Site 14				Site 15				Site 16	
Sample Code	RU07001	RU07002	RU07003	RU07004	RU07005	RU07006	RU07007	RU07008	RU07016	RU07017
Sample type	**RW**	**SED**	**SED**	**SED**	**RW**	**SED**	**SED**	**SED**	**RW**	**SED**
No. of organic compounds isolated	99	76	166	96	131	136	164	126	108	74
No. of reliably identified compounds (% of total)	18(18%)	31(41%)	50(30%)	39(41%)	22(17%)	70(51%)	61(37%)	62(49%)	18(17%)	35(47%)
PBDEs	-	(4)	(6)	(10)	-	(15)	(10)	(11)	-	(10)
PCBs	-	-	-	-	-	-	-	(24)	-	-
Chlorinated benzenes	-	(1)	(1)	(1)	-	(4)	(5)	-	-	(1)
Phthalate esters	1	-	-	-	2	-	-	-	2	1
DDT & metabolites	-	-	-	-	-	(2)	(1)	-	-	-
Substituted phenols	-	1	-	-	-			-	-	-
PAHs	-	4	19	11	-	19	13	4	-	1
Alkyl benzenes	-	3	-	-	-	-	1	-	-	-
Silicone containing compounds	-	1	-	-	-	-	-	1	-	-
Alkanes and alkenes	15	14	18	15	20	23	28	19	19	21
Other hydrocarbons	2	3	6	2	-	7	3	3	-	1

Table 16. Organic chemicals identified in river water (RW) and sediments (SED) from Neva River, St-Petersburg, Russia, 2007. The number of compounds reliably identified is presented for each group; (#) - signifies compounds identified at trace levels using a selective SIM method; n/a – not analysed; (-) – not detected.

Two sediment samples from site 15 (RU07006 & RU07007) contained DDT and its metabolites. Another sediment samples from the same site (RU07008) that was collected in the vicinity of the one of the famous Russian ship-museum “Aurora” contained a number of PCBs. Once again, specific sources of these toxic compounds to this part of the river are unknown, though it is likely that their presence results from historical applications and/or discharges as these compounds are highly persistent and may stay in the environment for a long period of time. However, even if representing legacy pollutants, such contamination of the river sediments remains of substantial concern, as PCBs that are taken up by aquatic organisms and fish accumulate in them, reaching levels that may be thousands of times higher than in water (ATSDR 2000). It is known that contaminated food is the main rout of human exposure to these chemicals, which have a number of toxic effects including reproductive and development disorders. More information on PCBs is presented in Box 3.

Contamination of the river sediments by heavy metals has also been in evidence, particularly in lower reaches of the Neva River where it flows through industrialised areas of St-Petersburg city. In contrast, sediment samples from the upstream sections of the Neva River (sites 11 and 12) did not contain any of the quantified metals at levels above typical background concentration ranges expected for uncontaminated surface water sediments.

Box 11. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons occur in a variety of materials such as soot, coal, tar, tobacco smoke, petroleum, and cutting oil. They are commonly found as product of incomplete combustion (DHHS 2000). It was shown that variety of PAHs (chrysene, benz[a]anthracene, benzo[c]phenanthrene, benzo[a]fluorene, benzo[b]fluorene, naphthalene, and benzofulvene) could be formed from indene in a flow reactor over a temperature range 650-8500C (Mingming & Mulholland 2001). The anthropogenic contribution usually outweighs the inputs from other sources. In recent study it was found that PCDD/Fs, PCBs and PCNs could be formed in de novo synthesis from PAHs in fluidized bed incinerators (Weber *et al*. 2001).

PAHs are prevalent pollutants in both terrestrial and aquatic environment that can cause a wide range of toxic effects. PAHs together with alkylbenzenes are considered to be the most toxic and are the highest in concentration in the initial phase of a crude oil spill (Overton, 1994). PAHs are toxic to soil organisms. It was shown that eight PAHs (naphthalene, acenaphthene, fluorene, acenaphthylene, anthracene, phenanthrene, pyrene, and fluoranthene) which have moderate lipophilocity (log Kow =3.3-5.2) are toxic to soil-dwelling springtail Folsomia fimetaria with a narcotic mode of toxic action (Sverdrup *et al*. 2002).

The toxicity of certain PAHs to aquatic organisms can be greatly increased upon exposure of the organisms to ultraviolet (UV) radiation present in sunlight (Monson *et al*. 1995, Ankley *et al*. 1995, Arfsten *et al*. 1996, McConkey *et al*. 1997). It was found that phototoxicity clearly was a function both of PAH dose and light intensity (Ankley *et al*. 1995; Huang *et al*. 1997). More recent investigations have shown that sunlight increases toxicity of both individual PAHs and PAH mixtures to marine organisms 1,000 times. This finding may explain widespread deformities seen in fish larvae in coastal waters and lead to greater pressure for reductions in emissions. Unlike organic contaminants such as dioxines and polychlorinated biphenyls, environmental levels of PAHs have shown little decline in recent years. Current PAH levels in air are estimated to be up to 20 times pre-industrial levels (ENDS 2000).

PAHs are harmful to human health. Individuals exposed by breathing or skin contact for long period of time to mixtures of PAHs and other compounds can develop cancer (ATSDR 1997). Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from a benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. Moreover, substitution of methyl groups on specific carbons of the ring also enhances carcinogenity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogens known (Williams 1986).

Fifteen PAHs have been reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity in experimental animals (DHHS 2000), they are:Benz[a]anthracene, Benzo[b]fluoranthene, Benzo[j]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]acridine, Dibenz[a,j]acridine, Dibenz[a,h]anthracene, Dibenzo[c,gh]carbazole, Dibenzo[a,e]pyrene, Dibenzo[a,h]p yreneDibenzo[a,i]pyrene, Dibenzo[a,l]pyrene, Indeno[1,2,3-cd]pyrene, and 5-methylchrysene.

Box 12. Chlorinated Benzenes

Chlorinated benzenes, or chlorobenzenes, are simple chlorinated derivatives of benzene, possessing between one and six chlorine atoms (i.e. mono- to hexachlorobenzene). Chlorobenzenes, especially mono-, di-, tri- and hexachlorinated forms, have had a variety of uses, including as solvents (e.g. in commercial PCB formulations) and intermediates in the manufacture of other chemicals such as antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. Hexachlorobenzene was used extensively as a pesticide, primarily as a wood preservative and fungicidal preparation for seeds (Budavari *et al*. 2000, ATSDR 2002). Today only mono- and dichlorobenzenes continue to be manufactured in substantial quantities.

Chlorobenzenes are relatively persistent in the environment and can bioaccumulate in both terrestrial and aquatic systems. Both acute and chronic effects have been reported in a wide range of aquatic organisms and in mammals. Effects of exposure vary depending on the chlorobenzene in question, though common impacts include those on the liver, thyroid and central nervous system (CNS). In general terms, toxicity tends to increase with increasing degree of chlorination (WHO 2004).

For example, human exposure to monochlorobenzene causes CNS depression and respiratory tract irritation, while animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al*. 1994). Effects reported for dichlorobenzenes in humans include anaemia, skin lesions, vomiting, headaches and eye and respiratory tract irritation (Ware 1988b). For tri- and tetrachlorobenzenes, impacts on liver, kidney and thyroid are among the most commonly reported in mammals (Giddings *et al*. 1994a, b). Some evidence for fetal and developmental toxicity has been reported for both tetra- and pentachlorobenzenes (Giddings *et al*. 1994c).

Hexachlorobenzene (HCB) is toxic to aquatic life, land plants, land animals, and humans. It is listed by the IARC as a Group 2B carcinogen, i.e. possible carcinogen to humans and also appears to be a tumour promoter. Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid, kidneys and CNS, with the liver and nervous system the most sensitive to its effects. (Newhook & Meek 1994, van Birgelen 1998, ATSDR 2002). HCB has been shown to be an endocrine disruptor in laboratory animal studies (Ralph *et al*. 2003). Furthermore, research suggests that HCB has dioxin-like toxicity (van Birgelen 1998) and that it could therefore make a substantial contribution to overall dioxin-type toxic effects in humans and wildlife (Pohl *et al*. 2001).

Hexachlorobenzene is the most regulated chemical among all chlorinated benzenes, and is included as one of twelve priority POPs covered by the 2001 Stockholm Convention on persistent organic pollutants (POPs). Pentachlorobenzene is one of the priority substances under the EU Water Framework Directive (EU 2001). Recently pentachlorobenzene was proposed as a candidate for inclusion in the UNECE Protocol on POPs (under the LRTAP Convention), based on its potential for long-range atmospheric transport, persistence (in water, sediment and soil), bioaccumulation and (eco)toxicity (van de Plassche *et al*. 2002).

For sites 13 and 14, sediment samples contained a range of metals at concentrations significantly higher than those found in the upstream sediments. At these sites, metal contamination profiles were broadly similar, including elevated levels of barium, chromium, copper, lead, nickel and zinc. At site 14, sediment was collected from both the Okhta River tributary at its junction with the Neva River (RU07004), as well as from the main Neva River immediately downstream of the river junction (RU07002). Metal levels in the Okhta River sediment were similar to those found in the Neva River at the upstream site 13. However, far higher levels of these metals were found at site 14 in the sediment from the main Neva River (RU07002), particularly for copper, lead and zinc. Furthermore, this sample contained a far greater range of metals at elevated levels, also including antimony, arsenic, cadmium, molybdenum and tin. Levels of many metals in this sample were tens to hundreds of times higher than those found in the upstream sediments (sites 11 & 12). The diverse range of metals in the Neva River sediment collected at site 14 indicates multiple current or historic inputs to the river in the vicinity. In contrst, additional sediment collected 500m further downstream (RU07003) contained elevated concentrations of only copper and zinc, and at a far lower level than that in the sediment collected close to the river junction (RU07002). This could simply reflect patchiness of contaminant distribution in the river sediments, a phenomenon which would require more detailed sampling to resolve.

River water collected at the junction of the Okhta and Neva Rivers at site 14 did not contain elevated levels of metals; river water from the main Neva River was not collected from this site.

Further downstream, at sites 15 and 16, the sediment samples contained far lower levels of most metals compared to those found in the most contaminated samples from site 14, though two sediments from site 15 did contain some metals at concentrations significantly higher than those found at the upstream sites 11 & 12. At site 15, sediment samples collected from the right bank of the Neva River (RU07007) and from a side branch of the main river (RU07008) both contained elevated levels of barium, chromium, copper, lead and zinc. The sediment from the side branch also contained mercury at a higher level than found in all other sediment samples (1.1mg/kg). Another sediment collected from the Neva River at the same site as RU07007, though from the left bank of the river (RU07006), did not contain metals at levels significantly higher than those in the upstream sediments from sites 11 and 12. This was also true for the sediment collected at site 16 (RU07017).

In general, river water samples collected at all sites from 11 to 16 contained straight chain alkanes and phthalate esters (DiBP and DnBP). The Neva River has intensive navigation from spring to autumn and, as a result of this, petroleum hydrocarbons are very likely to be present in the river waters as a result of leakage from the engines of ships and boats. Phthalate esters, broadly used as plasticizers for plastics such as PVC, are well known contaminants that have been detected in many environmental compartments including river water, to which they can enter from various sources. These results therefore indicate a background of contamination with these common pollutants.

None of the river water samples contained any of the quantified metals at levels above than their typical background concentration ranges found in uncontaminated surface water environments. Somewhat higher concentrations of iron, manganese and barium were found at site 14 (Okhta River, RU07001), compared to the other sites, which may result from the re-suspension of fine sedimentary particles into the water due to the mixing of the Okhta River and the Neva River at their junction where this sample was collected.

Conclusions

6

Underwater effluent dispersing pipe of Central WWTP, located at Nevskaya Guba, Gulf of Finland, St-Petersburg, Russia, 2007. © Greenpeace

The main finding of the current sdudy can be summerised as follows:

- PBDEs have been detected in all solid samples considered in this study (sediment, sludge, and soils samples), in one wastewater sample (RU07022) from Pirogovskaya embankment industrial zone and in one leachate/surface water sample (RU07024) from South Municipal Waste Landfill.
- PAHs have been detected in all river sediment samples.
- PCBs have been detected in three samples - in the sediment sample RU07008 (Neva River – site 15); in sediment sample RU07010 from Okhta River in the vicinity of the 1st pipe from JSC "Electropult" (site 1); and in the soil sample RU07035 from open e-wastes burning place (Site 8).
- Chlorobenzenes detected in many river sediment samples, in soil samples from open e-wastes burning sites and in sludges from WWTPs.
- Phthalate esters have been detected in samples from sites 1-3 (electronics production), site 5B (sewage sludge from Polygon Severny), and site 6 (wastewater from Central WWTP).
- Short chain chlorinated alkanes have been detected in soil sample RU07037 from the place of an unofficial e-wastes burning (site 10).
- Volatile chlorinated hydrocarbons were detected at elevated levels in wastewaters from two locations: chloroform and tetrachloromethane in sample from JSC "Electropult" plant (RU07009) and chloroform in samples from "Ladoga" plant (RU07033 & RU07043).
- Wastewater sample RU07011 from site 1 (electronics production, JSC "Electropult") had the highest concentration of toxic metals such as cadmium, chromium, copper, nickel, tin and zinc. Both cadmium and copper have been detected at over 50 times typical background levels for surface waters, nickel and zinc - elevated by over 20 times.
- Levels of antimony, cadmium, copper, lead and zinc were very elevated in all four soil samples from e-waste burning sites, with the highest in the soil sample RU07038 from site 10 in which cadmium was present at 250mg/kg. The concentrations of all these metals in these four samples far exceeded those typically seen in uncontaminated soils, ranging from tens to hundreds of times typical background levels.

Overall, this 'snapshot' study has shown that environmental contamination of the Neva River basin with metals and persistent organic pollutants is a widespread and, in many cases, ongoing problem. Current inputs include both direct discharges from industrial facilities engaged in the manufacture of electrical and electronic equipment and effluents discharged indirectly to one of the large common wastewater treatment plants located around the city. Even where cleanup of the wastewater is apparently being effective at removing such contaminants from the effluent finally disposed of to sea, evidence suggests that this is simply creating additional hazardous waste streams in the form of sludges, which are adding to the legacy of pollution in landfills and sludge disposal sites. At the same time, the dangerous and unregulated practice of open burning of electrical and electronic wastes to recover precious metals, commonplace in several areas of St-Petersburg, is generating further hotspots of contamination with toxic and environmentally persistent pollutants.

Greater monitoring and control of the generation and disposal of industrial wastes in the St-Petersberg region are clearly urgent priorities for protection of the environment and, ultimately, of the supplies of drinking water on which the city depends. This study serves as an indication of the diversity and scale of contaminant releases, which can be used in the first instance to target further study and identification of point sources of pollution. In that way, the problems identified here can begin to be tackled more effectively through measures taken at source, such as through the implementation of clean production techniques and the replacement of hazardous processes, chemicals and materials with safer alternatives. Ultimately, such approaches are far more sustainable, in environmental, social and economic terms, than continuing to generate huge volumes of contaminated water and solids which simply move pollution from one environmental compartment to another.

In relation to the manufacture and recycling or disposal of electrical and electronic equipment, recent and ongoing legislative developments within the European Union (in the form of the WEEE and associated RoHS Directives) have led to substantial steps forward in avoiding the use of hazardous chemicals such as lead, cadmium and PBDEs in such products, reducing the impacts of all stages in their lifecycle and making take-back and proper recycling of obsolete equipment more and more feasible. The development of equivalent controls within Eastern Europe, including in the Russian Federation, would clearly be a justifiable and highly effective contribution to tackling the growing environmental and health burdens of the electronic age.

7. References

Alaee, M., Arias, P., Sjödin, A & Bergman, A. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possibly modes of release. Environment International 29 (6): 683-689

Allchin, C. & Morris, S. (2002) The determination and occurrence of three groups of brominated flame retardants (polybrominated diphenyl ethers, tetrabromobisphenol A and hexabromocyclododecane) in samples of aquatic origin from the UK. In: Readman, J.;Worsfold, P., eds. Proceedings of ISEAC 32, International Symposium on the Environment and Analytical Chemistry, Plymouth, 17-20 June 2002: 15

Alloway, B.J. (1990) Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

Allsopp, M., Erry, B., Santillo, D. and Johnston, P. (2001) POPs in the Baltic: A review of persistent organic pollutants (POPs) in the Baltic Sea. Greenpeace, April 2001. ISBN 9-73361-71-0

Allsopp, M., Erry, B., Santillo, D. and Johnston, P. (2001a) POPs in the Baltic: A review of persistent organic pollutants (POPs) in the Baltic Sea. Greenpeace, April 2001. ISBN 9-73361-71-0

Allsopp, M., Erry, B., Stringer, R., Johnston, P. and Santillo, D. (2000) Recipe for Disaster: A review of persistent organic pollutants in food. Greenpeace, March 2000. ISBN 90-73361-63-X

Allsopp, M., Santillo, D., Johnston, P. and Stringer, R. (1999) The Tip of the Iceberg: State of knowledge of persistent organic pollutants in Europe and the Arctic. Greenpeace, August 1999. ISBN: 90-73361-53-2

Andrewes, P., KitChendian, K.T. and Wallace, K. (2004) Plasmid DNA damage caused by stibine and trimethylstibine. Toxicology and Applied Pharmacology 194: 41-48

Ankley G.T., Erickson R.J., Phipps G.L., Mattson V.R., Kosian P.A., Sheedy B.R., Cox J.S. (1995) Effects of light-intensity on the phototoxicity of fluoranthene to a benthic macroinvertebrate. Environmental Science and Technology 29 (11): 2828-2833

Arfsten D.P., Schaeffer D.J., Mulveny D.C. (1996) The effects of near-ultraviolet radiation on the toxic effects of polycyclic aromatic-hydrocarbons in animals and plants - a review. Ecotoxicology and Environmental Safety 33 (1): 1-24

Asplund, L., Athanasiadou, M., Sjödin, A., Bergman, Å. & Borjeson, H. (1999b) Organohalogen substances in muscle, egg and blood from healthy Baltic salmon (Salmo salar) and Baltic salmon that produced offspring with the M74 syndrome. Ambio 28(1): 67-76

Asplund, L., Hornung, M., Peterson, R.E,Turesson, K. & Bergman, Å. (1999a) Levels of polybrominated diphenyl ethers (PBDEs) in fish from the Great Lakes and Baltic Sea. Organohalogen Compounds 40:351-354

ATSDR (1997) Toxicological Profiles. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1999) Toxicological Profile for cadmium. United States Public Health Service, Agency for Toxic Substances and Disease Registry, July 1999

ATSDR (2000) Toxicological profile for polychlorinated biphenyls (PCBs), United States Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR (2002) Toxicological profile for hexachlorobenzene, United States Public Health Service, Agency for Toxic Substances and Disease Registry

ATSDR (2004) Toxicological Profile for copper. United States Public Health Service, Agency for Toxic Substances and Disease Registry, September 2004

ATSDR (2005a) Toxicological profile for tin, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2005

ATSDR (2005b) Toxicological profile for nickel. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2005

ATSDR (2007a) Toxicological profile for barium, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007

ATSDR (2007b) Toxicological Profile for lead. United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007

Bellinger, D. & Dietrich, K.N. (1994) Low-level lead exposure and cognitive functioning in children. Pediatric Annals 23: 600-605

Bi, X., Thomas, G.O., Jones, K.C., Qu, W., Sheng, G., Martin, F.L. & Fu, J. (2007) Exposure of Electronics Dismantling Workers to Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, and Organochlorine Pesticides in South China. Environmental Science and Technology 41(16): 5647-5653

Birnbaum, L.S. & Staskal, D.F. (2004). Brominated flame retardants: cause for concern? Environmental Health Perspectives 112 (1): 9-17

Blount, B.C., Silva, M.J., Caudill, S.P., Needham, L.L., Pirkle, J.L., Sampson, E.J., Lucier, G.W., Jackson, R.J. & Brock, J.W. (2000) Levels of seven urinary phthalate metabolites in a human reference population. Environmental Health Perspectives 108(10): 979-982

Branchi I., Capone F., Alleva E. & Costa L.G. (2003). Polybrominated Diphenyl ethers: neurobehavioural effects following developmental exposure. NeuroToxicology 24 (3): 449-462

Brigden, K., Labunska, I., Santillo, D. & Allsopp, M. (2005) Recycling of electronic wastes in China and India: workplace and environmental contamination. Greenpeace Research Laboratories Technical Note 09/2005, Publ. Greenpeace International, August 2005: 56 pp. (+ 47 pp. appendices)

Brigden, K., Santillo, D., Labunska, I. & Johnston, P. (2006) The toxic legacy: e-waste recycling in China and India. Public Service Review: International Development1: 84-86

Brigden, K., Labunska, I., Santillo, D.,Walters, A. (2007) Cutting edge contamination: A study of environmental pollution during the manufacture of electronic products. Greenpeace Research Laboratories Technical Note 01/2007, Publ. Greenpeace International, February 2007: 79 pp.(+ 8 pp.)

Brouwer, A., Longnecker, M.P., Birnbaum, L.S., Cogliano, J., Kostyniak, P., Moore, J., Schantz,S. & Winneke, G. (1999) Characterization of potential endocrine-related health effects at low-dose levesl of exposure to PCBs. Environ. Health Persp. 107(Suppl. 4): 639-649

Bryan, G.W. and Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environmental Pollution 76: 89-131

Budavari, S., O'Neil, M., Smith, A., Heckleman, P. & Obenchain, J. [Eds] (2000) The Merck index. 12th Edition, on CD_ROM, Version 12:3. Merck & Co., Inc.

Butte, W. & Heinzow, B. (2002) Pollutants in house dust as indicators of indoor contamination. Reviews in Environmental Contamination and Toxicology 175: 1-46

Canfield, R.L., Henderson, C.R., Cory-Slechta, D.A., Cox, C., Jusko, T.A., Lanphear, B.P. (2003) Intellectual impairment in children with blood lead concentrations below 10 mu g per deciliter. New England Journal of Medicine 348(16): 1517-1526

CNREP (2006) Protection of the environment, management of natural resources and ecological safety in St-Petersburg in 2005. Golubev, D.A. & Sorokin, N.D. [Eds]. Committee on Natural Resources and Environmental Protection (CNREP), SPb, 492pp.

Colon, I., Caro, D., Bourdony, C.J. & Rosario, O. (2000) Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. Environmental Health Perspectives 108(9): 895-900

Corrales, T., Catalina, F. , Peinado, C. &Allen, N.S. (2003) Free radical macrophotoinitiators: an overview on recent advances. Journal of Photochemistry and Photobiology A: Chemistry 159:103–114

CSTEE (2001) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate - Report version (Human Health Effects): Final report, May 2001. Opinion expressed at the 27th CSTEE plenary meeting, Brussels, 30 October 2001: 7 pp. de Boer, J.,Wester, P.G., Klamer, H.J.C., Lewis, W.E. & Boon, J.P. (1998) Do flame retardants threaten ocean life? Nature 394 (2 July): 28-29

CSTEE (2002) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on "Short-Chain Chlorinated Paraffins (SCCPs)", Follow-up of Directive 2002/45/EC (Opinion expressed at the 35th CSTEE plenary meeting, Brussels, 17 December 2002): 8 pp. http://europa.eu.int/comm/food/fs/sc/sct/out174_en.pdf

Dalgaard, M., Nellemann, C., Lam, H.R., Sorensen, I.K. & Ladefoged, O. (2001) The acute effects of mono(2-ethylhexyl)phthalate (MEHP) on testes of prepubertal Wistar rats. Toxicology Letters 122: 69-79

Darnerud, P.O. (2003). Toxic effects of brominated flame retardants in man and in wildlife. Environment International 29 (6): 841-853

de Voogt, P. & Brinkman, U.A.Th. (1989) Production, properties and usage of polychlorinated biphenyls. In: Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxines and related products. Kimbrough, R.D. & Jensen, A.A. [Eds] Topics in environmental health, Vol.4. Publ. By Elsevier Science Publishers B.V.: 3-29

DHHS (2005) 11th Report on Carcinogens. U.S. Department of Health and Human Services, US Public Health Service, National Toxicology Program

EC (2000) European Union Risk Assessment Report, alkanes, C10-13, chloro, 1st Priority List, Volume 4, EUR 19010 EN: 176 pp.

EC (2005) Directive 2005/84/EC of the European Parliament and of the Council of 14 December 2005 amending for the 22nd time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (phthalates in toys and childcare articles). Official Journal of the European Communities L344, 27.12.2005: 40-43 http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:344:0040:0043:EN:PDF

EC (2006) Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, European Commission COM(2006) 397 final, Brussels, 17.7.2006

EEC (1986) Council Directive 86/280/EEC of 12 June 1986 on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC. OJ L 181: 16-27

EEC (1988) Council Directive 88/347/EEC of 16 June 1988 on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC. OJ L 158: 35-41

Elinder, C.G. & Jarup, L. (1996) Cadmium exposure and health risks: recent findings. Ambio 25, 5: 370-373

Ema, M. & Miyawaki, E. (2002) Effects on development of the reproductive system in male offspring of rats given butyl benzyl phthalate during late pregnancy. Reproductive Toxicology 16: 71-76

ENDS (2000) Sunlight increases PAH toxicity 1,000-fold, researchers find. The ENDS Report, 304:12

ENDS (2002) PVC Industry agrees to phase out lead stabilisers by 2015. The ENDS Report No. 328, May 2002, 31-32

Eriksson, P., Viberg, H., Jakobsson, E., Orn, U., Fredriksson, A. (2002) A brominated flame retardant, 2,2 ',4,4 ',5-pentabromodiphenyl ether: Uptake, retention, and induction of neurobehavioral alterations in mice during a critical phase of neonatal brain development.Toxicological Sciences 67(1): 98-103

Eriksson, P.,Viberg, H., Ankarberg, E., Jakobsson, E., Örn, U. & Fredriksson, A. (2001) Polybrominated diphenylethers (PBDEs): a novel class of environmental neurotoxicants in our environment. In: Asplund, L.; Bergman, Å.; de Wit, C., *et al*. eds. Proceedings of the Second International Workshop on Brominated Flame Retardants, BFR 2001, Stockholm, May 14-16 2001: 71-73

EU (1991) Directive 91/338/EEC of 18 June 1991 amending for the 10th time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations. Official Journal L 186, 12/07/1991: 59-63

EU (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for the Community action in the field of water policy. Official Journal L 327, 22/12/2000: 1-72

EU (2001) Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, Official Journal L 249, 17/09/2002: 27-30

EU (2002) Directive 2002/45/EC of the European Parliament and of the Council of 25 June 2002 amending for the twentieth time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (short-chain chlorinated paraffins), Official Journal L 177, 06/07/2002: 21-22

EU (2002a) Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Official Journal L 037, 13/02/2003: 19-23

EU (2002b) Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE) - Joint declaration of the European Parliament, the Council and the Commission relating to Article 9. Official Journal L 037, 13/02/2003: 24–39

EU (2003a) Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether), Official Journal L 42, 15/02/2003: 45-46

Farrar, D.G. (2000) Chlorinated paraffins – their toxicology and environmental effects and regulatory implications. Organohalogen Compounds 47: 129-130

Fisk, A.T., Tomy, G.T. & Muir, D.C.G. (1999) Toxicity of C-10-, C-11-, C-12- and C-14- polychlorinated alkanes to Japanese medaka (Oryzias latipes) embryos. Environmental Toxicology and Chemistry 18(12): 2894-2902

Flynn, H.C., Meharg, A.A., Bowyer, P.K. and Paton, G.I. (2003) Antimony bioavailability in mine soils. Environmental Pollution 124(1): 93-100

Fromme H., Lahrz T., Piloty M., Gebhart H., Oddoy A. & Rüden H. (2004) Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). Indoor Air 14 (3): 188-195

Geibig, J.R., Socolof, M.L. (2005) Solders in Electronics: A Life-Cycle Assessment. EPA744-R-05-001. University of Tennessee (UT) Center for Clean Products and Clean Technologies

Gerhardt, A. (1993) Review of impact of heavy-metals on stream invertebrates with special emphasis on acid conditions. Water air and soil pollution, 66(3-4): 289-314

Giddings, M., Meek, M.E. & Gomes, R. (1994a) Trichlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 517-525

Giddings, M., Meek, M.E. & Gomes, R. (1994b) Tetrachlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 473-481

Giddings, M., Meek, M.E. & Gomes, R. (1994c) Pentachlorobenzene: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 435-441

Goyer, R.A. (1996) Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766

Guo, Y.L., Lambert, G.H., Hsu, C-C. and Hsu, M.M.L. (2004) Yucheng: health effects of prenatal exposure to polychlorinated biphenyls and dibenzofurans. Int Arch Occup Environ Health 77: 153-158

Haave, M., Ropstad, E., Derocher, A.E., Lie, E., Dahl, E., Wiig, O., Skarre, J.U. and Jenssen, B.M. (2003) Polychlorinated biphenyls and reproductive hormones in female polar bears at Svalbard. Environmental Health Perspectives 111 (4): 431-436

Harrad, S.,Wijesekera, R., Hunter, S., Halliwell, C. & Baker R. (2004). Preliminary assessment of UK human dietary and inhalation exposure to polybrominated dipehyl ethers. Environmental Science and Technology 38 (8): 2345-2350

Hellstrom, L., Elinder, C.G., Dahlberg, B.,Lundberg, M., Jarup, L., Persson, B., & Axelson, O. (2001) Cadmium Exposure and End-Stage Renal Disease. American Journal of Kidney Diseases, 38(5), 1001 1008

Hites, R.A. (2004). Polybrominated Diphenyl ethers in the environment and in people: A meta-analysis of concentrations. Environment, Science and Technology 38 (4): 945-956

Huang X.D., McConkey B.J., Babu T.S., Greenberg B.M. (1997) Mechanisms of photoinduced toxicity of photomodified anthracene to plants: Inhibition of photosynthesis in the aquatic higher plant Lemna gibba (duckweed). Environmental Toxicology and Chemistry 16 (8): 1707-1715

Huo, X., Peng, L., Xu, X., Zheng, L., Qiu, B., Qi, Z., Zhang, B., Han, D. & Piao, Z. (2007) Elevated Blood Lead Levels of Children in Guiyu, an Electronic Waste Recycling Town in China. Environmental Health Perspectives 115 (7):113-117

IARC (1990) Nickel and certain nickel compounds. In: International Agency for Research on Cancer (IARC) monographs on the evaluation of the carcinogenic risk of chemicals to humans. Volume 49; Chromium, Nickel and Welding. ISBN 9283212495

Ikonomou, M.G., Rayne, S. & Addison, R.F. (2002) Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. Environmental Science and Technology 36(9): 1886-1892

IPCS (1998) Polybrominated dibenzo-p-dioxins and dibenzofurans, Environmental Health Criteria, No. 205, International Programme on Chemical Safety, UNEP/ILO/WHO, ISBN 92 4 157205 1: 303 pp.

Jenkins, R.O., Morris, T.A., Craig, P.J., Goessler, W., Ostah, N. and Wills, K.M. (2000) Evaluation of cot mattress inner foam as a potential site for microbial generation of toxic gases. Human and Experimental Toxicology 19(12): 693-702

Jones, A., Hedgecott, S. & Zabel, T.F. (1988) Information related to proposed "Red List" substances WRC Report PRU 1901-M/2 73pp

Kentner, M., Leinemann, M., Schaller, K.H., Weltle, D. and Lehnert, G. (1995) External and internal antimony exposure in starter battery production. International Archives of Occupational and Environmental Health 67(2): 119-123

Kim, H.A., Heo, Y., Oh, S.Y., Lee, K.J. and Lawrence, D.A. (1999) Altered serum cytokine and immunoglobulin levels in the workers exposed to antimony. Human and Experimental Toxicology 18(10): 607-613

Koh, I-.O., Rotard, W. & Thiemann, W.H-.P. (2002) Analysis of chlorinated paraffins in cutting fluids and sealing materials by carbon skeleton reaction gas chromatography. Chemosphere 47: 219-227

Krachler, K. and Emons, H. (2001) Urinary antimony speciation by HPLC-ICP-MS. Journal of Analytical Atomic Spectrometry 16: 586-590

Lau, J.H., Wong, C.P., Lee, N.C. & Ricky Lee, S.W. (2003) Electronics Manufacturing with Lead-Free, Halogen-Free & Conductive-Adhesive materials. McGraw-Hill. ISBN 0071386246

Lees, P.S.J., Corn, M. & Breysse, P.N. (1987) Evidence for dermal absorption as the major route of body entry during exposure of transformer maintenance and repairmen to PCBs. Am. Ind. Hyg. Assoc. J. 48(3): 257-264

Legler, J. & Brouwer, A. (2003). Are brominated flame retardants endocrine disruptors? Environmental International 29 (6): 879-885

Li J., Shrivastava P., Gao Z. & Zhang H-C. (2004). Printed circuit board recycling. A state-of –the-art survey. IEEE Transactions on Electronics Packaging Manufacturing 27 (1): 33-42.

Liao, Ch-S., Yen, J-H., Wang, Y-Sh. (2006) Effects of endocrine disruptor di-n-butyl phthalate on the growth of Bok choy (Brassica rapa subsp. chinensis). Chemosphere 65 (2006) 1715–1722

Lindstrom, G., van Bavel, B., Hardell, L. & Liljegren, G. (1997) Identification of the flame retardants polybrominated diphenyl ethers in adipose tissue from patients with non-Hodgkin's lymphoma in Sweden. Oncology Reports 4(5): 999-1000

Lovekamp-Swan T. & Davis B.J. (2003) Mechanisms of phthalate ester toxicity in the female reproductive system. Environmental Health Perspectives 111 (2): 139-145

Malcoe, L.H., Lynch, R.A., Kegler, M.C. & Skaggs, V.J. (2002) Lead sources, behaviors, and socioeconomic factors in relation to blood lead of native American and white children: A community-based assessment of a former mining area. Environmental Health Perspectives 110 (Supplement 2): 221-231

Matthews, G. (1996) PVC: production, properties and uses. Publ: The Institute of Materials, London. ISBN: 0901716596

McConkey B.J., Duxbury C.L., Dixon D.G., Greenberg B.M. (1997) Toxicity of a PAH photooxidation product to the bacteria Photobacterium phosphoreum and the duckweed Lemna gibba: Effects of phenanthrene and its primary photoproduct, phenanthrenequinone. Environmental Toxicology and Chemistry 16 (5): 892-899

Meek, M.E., Giddings, M. & Gomes, R. (1994) Monochlorobenzene: evaluation of risks to health from environmental exposure in Canada. Environ. Carcin. Ecotox. Revs. 12(2): 409-415

Meerts, I.A.T.M., Letcher, R.J., Hoving, S., Marsh, G., Bergman, Å., Lemmen, J.G., van der Burg, B. & Brouwer, A. (2001) In vitro estrogenicity of polybrominated diphenyl ethers, hydroxylated PBDEs and polybrominated bisphenol A compounds. Environmental Health Perspectives 109(4): 399-407

Meerts, I.A.T.M., Marsh, G., van Leeuwen-Bol, I., Luijks, E.A.C., Jakobsson, E., Bergman, Å. & Brouwer, A. (1998) Interaction of polybrominated diphenyl ether metabolites (PBDE-OH) with human transthyretin in vitro. Organohalogen Compounds 37: 309-312

Meerts, I.A.T.M., Marsh, G., van Leeuwen-Bol, I., Luijks, E.A.C., Jakobsson, E., Bergman, Å. & Brouwer, A. (1998) Interaction of polybrominated diphenyl ether metabolites (PBDE-OH) with human transthyretin in vitro. Organohalogen Compounds 37: 309-312

Meironyte, D., Noren, K. & Bergman, Å. (1999) Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. Journal of Toxicology and Environmental Health - Part A 58(6): 329-341

Meneses, M., Wingfors, H., Schuhmacher, M., Domingo, J.L., Lindstrom, G. & von Bavel, B. (1999) Polybrominated diphenyl ethers detected in human adipose tissue from Spain. Chemosphere 39(13): 2271-2278

Mingming,L. & Mulholland, J.A. (2001) Aromatic hydrocarbon grows from indene. Chemosphere 42(5-7):625-633

Monson P.D., Ankley G.T., Kosian P.A. (1995) Phototoxic response of lumbriculus-variegatus to sediments contaminated by polycyclic aromatic-hydrocarbons. Environmental Toxicology and Chemistry 14 (5): 891-894

Musson, S.E., Jang, Y.C., Townsend, T.G. & Chung, I.H. (2000) Characterization of lead leachability from cathode ray tubes using the toxicity characteristic leaching procedure. Environmental Science & Technology 34(20): 4376-4381

Mylchreest, E., Sar, M.,Wallace, D.G. & Foster, P.M.D. (2002) Fetal testosterone insufficiency and abnormal proliferation of Leydig cells and gonocytes in rats exposed to di(n-butyl) phthalate. Reproductive Toxicology 16: 19-28

Newhook, R. & Meek, M.E. (1994) Hexachlorobenzene: Evaluation of risks to health from Environmental Exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 345-360

Nor, Y.M. (1987) Ecotoxicity of copper to aquatic biota: a review. Environmental Research, 43: 272-282

OECD (2003) Technical guidance for the environmentally sound management of specific waste streams: used and scrap personal computers. Organisation for Economic Co-operation and Development (OECD) Working Group on Waste Prevention and Recycling. ENV/EPOC/WGWPR(2001)3/FINAL.

Olsman, H., Engwall, M., Kammann, U., Klempt, M., Otte, J., van Bavel, B., Hollert, H. (2007) Relative differences in aryl hydrocarbon receptor–mediated response for 18 polybrominated and mixed halogenated dibenzo-p-dioxins and -furans in cell lines from four different species. Environmental Toxicology & Chemistry 26(11), 2448-2454

Olsson, I.M., Eriksson, J., Öborn, I., Skerfving, S., & Oskarsson, A. (2005) Cadmium in Food Production Systems: A Health Risk for Sensitive Population Groups. Ambio, 34(4): 344-351

OSPAR (1998) OSPAR Strategy with Regard to Hazardous Substances, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR 98/14/1 Annex 34

OSPAR (2001) Short Chain Chlorinated Paraffins, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London, ISBN 0-946956-77-4: 16 pp.

Otake,T., Yoshinaga, J. & Yanagisawa, Y. (2001) Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. Environmental Science and Technology 35(15): 3099-3102

Overton (1994) Toxicity of petroleum. In: Basic Environmental Toxicology. Cockerham & Shane [Eds], Chapter 5, pp. 133-156

PARCOM (1995) PARCOM Decision 95/1 on the Phasing Out of Short Chained Chlorinated Paraffins, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London: 3 pp.

Patterson, T.J., Ngo, M., Aronov, P.A., Reznikova, T.V., Green, P.G. and Rice, R.H. (2003) Biological activity of inorganic arsenic and antimony reflects oxidation state in cultured human keratinocytes. Chemical Research in Toxicology 16(12): 1624-1631

Peltola, J. & Yla-Mononen, L. (2001) Pentabromodiphenyl ether as a global POP. TemaNord 2001:579, Nordic Council of Ministers, Copenhagen, ISBN 92-893-0690-4: 78 pp.

Peters, A.J., Tomy, G.T., Jones, K.C., Coleman, P. & Stern, G.A. (2000) Occurrence of C10-C13 polychlorinated n-alkanes in the atmosphere of the United Kingdom. Atmospheric Environment 34: 3085-3090

Pohl, H.R., McClure, P.R., Fay, M., Holler, J. and DE Rosa, C.T. (2001) Public health assessment of hexachlorobenzene 43 (4-7): 903-908

Private Communication (2007) Letter from St-Petersburg's Committee on the Management of Natural Resources, Environmental Protection and Ecological Safety, from 25.06.2007, Nr. 02-1316/07-0-0, St-Petersburg, Russia

Qu, W., Bi, X., Sheng, G., Lu, S., Fu, J., Yuan, J. & Li, L. (2007) Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. Environment International. 33 (8): 1021-1028

Ralph, J.L., Orgebin-Crist, M-C., Lareyre, J-J. and Nelson, C.C. (2003) Disruption of androgen regulation in the prostate by the environmental contaminant hexachlorobenzene. Environmental Health Perspectives 111 (4): 461-466

Rice, D.C. (1999) Behavioral impairment produced by low-level postnatal PCB exposure in monkeys. Environmental Research Section A 80: S113-S121

Sadiq, M. (1992) Toxic metal chemistry in marine environments. Marcel Dekker Inc., New York, Basel, Hong Kong. ISBN 0824786475

Safe, S.H. (1993) Polychlorinated biphenyls. IN: Kroschwitz, J.I. & Howe-Grant, (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition .Publ. Wiley-Interscience, N.Y. Volume 6: 127-139

Salomons, W. & Forstner, U. (1984) Metals in the hydrocycle. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, ISBN 3540127550

Santillo, D., Labunska, I., Davidson, H., Johnston, P., Strutt, M. & Knowles, O. (2003a) Consuming Chemicals: Hazardous Chemicals in house dust as an indicator of chemical exposure in the home: Part I - UK. Greenpeace Research Laboratories Technical Note 01/2003, April 2003: 74 pp.

Santillo, D., Labunska, I., Fairley, M. & Johnston, P. (2003b) Hazardous chemicals in house dusts as indicators of chemical exposure in the home: Part II – Germany, Spain, Slovakia, Italy and France. Greenpeace Research Laboratories Technical Note 02/2003, December 2003: 96 pp.

Sauve, S., McBride, M.B. & Hendershot, W.H. (1997) Speciation of lead in contaminated soils. Environmental Pollution 98(2): 149-155

Schutz, A., Olsson, M., Jensen, A., Gerhardsson, L., Borjesson, J., Mattsson, S., & Skerfving, S. (2005) Lead in finger bone, whole blood, plasma and urine in lead-smelter workers: extended exposure range. International Archives of Occupational and Environmental Health 78(1): 35-43

Seegal, R.F. & Shain, W. (1992) Neurotoxicity of polychlorinated biphenyls. The role of ortho-substituted congeners in altering neurochemical function. IN: The vulnerable brain and environmental risks, volume 2: Toxins in food, Isaacson, R.L. & Jensen, K.F., Eds. Publ: Plemin Press: 169-195

She, J.,Winkler, J.,Visita, P., McKinney, M. & Petreas, M. (2000) Analysis of PBDEs in seal blubber and human breast adipose tissue samples. Organohalogen Compounds 47: 53-56

Silva, M.J., Barr, D.B., Reidy, J.A., Malek, N.A., Hodge, C.C., Caudill, S.P., Brock, J.W., Needham, L.L. & Calafat, A.M. (2004) Urinary levels of seven phthalate metabolites in the U.S. population from the National Health and Nutrition Examination Survey (NHANES) 1999-2000. Environmental Health Perspectives 112 (3): 331-338

Sjödin, A., Carlsson, H.,Thuresson, K., Sjolin, S., Bergman, Å. & Ostman, C. (2001) Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environmental Science and Technology 35(3): 448-454

Sjödin, A., Patterson, D.G. and Bergman, A. (2003). A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29: 829-839

Stern, G.A. & Tomy, G. (2000) An overview of the environmental levels and distribution of polychlorinated paraffins. Organohalogen Compounds 47: 135-138

Strandman, T., Koistinen, J., Kiviranta, H., Vuorinen, P.J., Tuomisto, J. & Vartiainen, T. (1999) Levels of some polybrominated diphenyl ethers (PBDEs) in fish and human adipose tissue in Finland. Organohalogen Compounds 40:355-358

Sverdrup, L.E., Nielsen, T. & Krogh, P.H. (2002) Soil ecotoxicity of polycyclic aromatic hydrocarbons in relation to soil sorption, lipophilicity, and water solubility. Environ. Sci. Technol. 36(11):2429-2435

Swami, K., Narang, A.S., Narang, R.S. & Eadon, G.A. (1992) Thermally induced formation of PCDD and PCDF from tri- and tetrachlorobenzene in dielectric fluids. Chemosphere 24(12): 1845-1853

Swan, S.H., Main, K.M., Liu, F., Stewart, S.L., Kruse, R.L., Calafat, A.M., Mao, C.S., Redmon, J.B., Ternand, C.L., Sullivan, S. & Teague, J.L. (2005) Decrease in anogenital distance among male infants with prenatal phthalate exposure. Environmental Health Perspectives 113 (8): 1056-1061

Swedish EPA (1999) Persistent Organic Pollutants. A Swedish view of an International Problem. Text:Claes Bernes. ISBN 91-620-1189-8

Thomsen, C., Lundanes, E. & Becher, G. (2002) Brominated flame retardants in archived serum samples from Norway: A study on temporal trends and the role of age. Environmental Science and Technology 36(7): 1414-1418

Tomy, G.T., Stern, G.A., Lockhart, W.L. & Muir, D.C.G. (1999) Occurrence of C-10-C-13 polychlorinated n-alkanes in Canadian mid-latitude and arctic lake sediments. Environmental Science and Technology 33(17): 2858-2863

Train, R.E. (1979) Quality criteria for water. Castle House Publications 256pp

UNEP (2006) Advance Report of the second meeting of the Persistent Organic Pollutants Review Committee (POPRC), 6 -10 November 2006, Geneva, Switzerland: 48 pp. http://www.pops.int/documents/meetings/poprc_2/meeting_docs/report/default.htm

USEPA (1998) Printed Wiring Board Pollution Prevention and Control Technology: Analysis of Updated Survey Results EPA-744-R-98-003

van Birgelen, A.P.J.M. (1998) Hexachlorobenzene as a possible major contributor to the dioxin activity of human milk. Environ. Health Persp. 106(11): 683-688

van de Plassche, E., Schwegler, A., Rasenberg, M. & Schouten G. (2002) Pentachlorobenzene. Report presented at the Third Meeting of the POPs Expert Group in Geneva, Switzerland, in June 2002, available at http://www.unece.org/env/popsxg/pentachloorbenzeen.pdf

Viberg, H., Fredriksson, A., Eriksson, P. (2004) Investigations of strain and/or gender differences in developmental neurotoxic effects of polybrominated diphenyl ethers in mice. Toxicological Sciences 81(2): 344-353

Ware, G.W. (Ed.)(1988a) Chlorobenzene. Rev. Environ. Contam.Toxicol. 106: 37-49

Ware, G.W. (Ed.)(1988b) Ortho-, meta- and para- dichlorobenzene. Rev. Environ. Contam.Toxicol. 106: 51-56

Weber, R., Iino, F., Imagawa, T., Takeuchi, M., Sakurai, T. & Sadakata, M. (2001) Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: Mechanistic aspects and correlation to fluidized bed incinerators. Chemosphere 44(6): 1429-1438

Weisglas-Kuperus, N., Vreugdenhil, H.J.I. and Mulder, P.G.H. (2004) Immunological effects of environmental exposure to polychlorinated biphenyls and dioxins in Dutch school children. Toxicological Letters 149: 281-285

White, G.P., Mathias, C.G.T. and Davin, J.S. (1993) Dermatitis in workers exposed to antimony in a melting process. Journal of Occupational and Environmental Medicine 35(4): 392-395

WHO (2004) Chlorobenzenes other than hexachlorobenzene: environmental aspects. Concise international chemical assessment document: 60. ISBN 92 4 153060 X, ISSN 1020-6167, Geneva 2004

Williams G.M., Weisburger J.H. (1986) Chemical carcinogens. In Toxicology: the basic science of poisons. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 99-173

Williams, E. (2004) Environmental impacts of microchip manufacture. Thin Solid Films, 461: 2– 6

World Health Organisation (1989) Lead; environmental aspects. Environmental Health Criteria 85. ISBN 9241542853

World Health Organisation (1992) Cadmium. Environmental Health Criteria 135. ISBN 9241571357

World Health Organisation (2006) Guidelines for drinking-water quality, Volume 1, recommendations; 3rd edition. World Health Organization (WHO). ISBN 9241546964. www.who.int/water_sanitation_health/dwq/gdwq0506.pdf

8. Appendix

A1. Analysis for organic compounds

A1.1. Volatile Organic Compounds (VOCs) analysis

For volatile organic compound analysis, no sample preparation was required. The original sample was sub-sampled immediately after opening. Three portions of 10ml each were transferred into 20ml headspace vials and sealed with Teflon-lined vial caps. One sub-sample was used for the organic screen analysis to evaluate the whole range of volatile compounds in the sample. Two sub-samples were used as duplicates for quantitative analysis of a range of halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method. All standard compounds were obtained from Sigma-Aldrich Co. Ltd./Supelco UK.

VOCs were analysed using an Agilent 6890 gas chromatograph with Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler interfaced with an Agilent Enhanced Chem-Station data system and linked to an Agilent 5973N MSD operated in EI mode. GC oven temperature program was: 350C (hold for 4min), raised to 550C at 50C/min, and then to 2100C at 150C/min. Carrier gas was helium at 1ml/min.

Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated for each quantified compound (Table A).

Compound	Limit of quantification (LOQ), µg/l	SD, µg/l	RSD, %	Correlation coefficient, r2
Chloroform	0.5	0.06	2.8	0.999
Ethane, 1,1,1-trichloro-	0.2	0.08	4.0	0.999
Ethane, 1,1-dichloro-	0.5	0.13	5.9	0.999
Ethane, 1,2-dichloro-	1.0	0.21	9.4	1.000
Ethane, 1,1,2,2-tetrachloro-	0.2	0.13	6.7	1.000
Ethene, tetrachloro-	0.2	0.07	3.4	0.999
Methane, bromodichloro-	0.5	0.09	3.7	0.997
Methane, dichloro-	0.5	0.08	3.7	0.999
Methane, tetrachloro-	0.2	0.06	3.1	0.999

Table A. Standard deviation (SD) and relative standard deviation (RSD) calculated using concentration of the seven replicas of the standard mixture containing 2ppb of each analyte. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r2 – corresponding correlation coefficient) used for quantification.

A number of blanks of laboratory air capped at the time of sub sampling were also analysed alongside ultra pure reagent water which was used for standard calibration solutions preparation. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analysing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS.

A.1.2. Semi-volatile Organic Compounds analysis

20 µg of Internal Standard (IS) deuterated naphthalene was added to each portion of sample that was a subject to extraction. For sediment samples, approximately 30 g of each sample was extracted twice using 15ml pentane and 5ml acetone at 69oC with sonication for 2h, once at original pH and once following acidification to pH 2 with nitric acid (10% v/v). Water samples (approximately 1000ml) were extracted, with agitation, for 2 hours twice with 20ml portions of pentane, once at original pH and once after acidification to pH 2 with using nitric acid (10% v/v).

Clean-up procedure was the same for aqueous and sediment samples. For each sample, the two extracts obtained were combined, concentrated to 3ml, shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left for separation. The pentane phase was collected and eluted through a Florisil column using a 95:5 pentane:toluene mixed eluent and concentrated to 2ml. Particularly oily extracts were treated with concentrated sulphuric acid prior to TBA-reagent clean-up. 20 µg of IS bromonaphthalene was added to each extract prior to GC/MS analysis.

Samples were analysed using an Agilent 6890 Series gas chromatograph with a Restek Rtx-XLB column (30m , 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced

Chem Station data system. GC oven temperature program was: 35°C, raised to 260°C at 10°C/min, then to 295°C at 50°C/min (hold for 5min), then to 325°C at 50°C/min (hold for 12min), and then to 330°C at 50°C/min (hold for 4min). Carrier gas was helium at 2ml/min. Identification of compounds was carried out by matching spectra against Agilent Wiley7N and Pesticides Libraries. Additionally, spectra and retention time of compounds isolated from the samples were matched against those obtained during GC/MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons. Analysis for PBDEs was additionally carried out using an Agilent 6890 Series gas chromatograph with a Restek Rxi-5MS column (15m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in NCI mode.

A2. Analysis for metals and metalloids

A2.1. Preparation

Sediment and soil samples were air dried to constant weight, homogenised, and sieved through a 2mm mesh and ground to a powder. Approximately 0.5g of sample was digested with 7.5ml concentrated hydrochloric acid, 2.5 ml concentrated nitric acid and 10 ml de-ionised water, firstly overnight at room temperature, then for 4 hours under reflux at 130°C. Digests were filtered and made up to 50ml.

Water samples (100ml) were acidified with nitric acid (10% v/v). 50ml of each acidified sample was refluxed at 130°C for 4 hours. Digests were filtered and made up to 50ml.

A2.2. Analysis

Prepared samples were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 1 mg/l and 10 mg/l, and matrix matched for the samples, were used for instrument calibration.

Mercury (Hg) was sepatately determined using Cold Vapour Generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid for solid samples or 10% v/v nitric acid for aqueous samples). The calibration was validated using a quality control standard (80 µg/l), prepared internally from different reagent stock.

A2.3. Quality control

For solid samples, 3 samples were prepared in duplicate and analysed to verify method reproducibility along with identically prepared blanks. To check the method efficiency certified reference material (CRM) samples were prepared in an identical manner (GBW07406, yellow-red soil, certified by the China National; Analysis Centre for Iron and Steel, Beijing, China; GBW07311, stream sediment, certified by the China National Analysis Centre for Iron and Steel). For the water samples, 2 samples were prepared in duplicate along with a blank sample and a mixed metal solution of 8 mg/ l, other than mercury at 80 µg/l. These control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards prepared from different reagent stocks to the instrument calibration standards; 8 mg/l for solid sample calibration, 8 mg/l and 0.8 mg/l for water sample calibration.

Further details of the methods employed can be provided on request.

Greenpeace is
an independent
global campaigning
organisation that acts
to change attitudes
and behaviour, to
protect and conserve
the environment and
to promote peace.