RUSSIAN REFUSE III

Investigation of organic and heavy metal contaminants input and distribution in selected rivers of the Russian Federation

Iryna Labunska, Kevin Brigden, David Santillo, Alexey Kiselev & Paul Johnston

Greenpeace Research Laboratories Technical Note 04/2011

Contents

Introduction....3
Sampling program and description of sampling sites....4
Leningradskaya Oblast Rivers Syas and Svir`. Krasny Bor toxics waste landfill....4
Vologodskaya oblast. Cherepovets, Rivers Koshta, Sheksna and Yagorba....6
Yaroslavl Oblast. Yaroslavl, Rybinsk and River Volga....9
Moscow and River Moskva....11
Results and discussion....12
Leningradskaya oblast. Rivers Syas and Svir`. Krasny Bor toxics waste landfill....13
Vologodskaya oblast. Cherepovets, Rivers Koshta, Sheksna and Yagorba....18
Yaroslavl Oblast. Yaroslavl, Rybinsk and River Volga....20
Moscow and River Moskva....23
Conclusions....26
Leningradskaya Oblast....26
Vologodskaya Oblast....27
Yaroslavlskay Oblast....27
Moscow....27
Appendix. Analytical methodology....29
Analysis for Volatile Organic Compounds (VOCs)....29
Analysis for extractable organic compounds....30
Analysis for metals....31

Introduction

Water pollution with hazardous chemicals is a significant problem in Russia. The country has a large industrial sector, which is still, almost 20 years after the collapse of the the Soviet Union, a significant source of pollution. The regulatory framework is highly inadequate meaning that regulation is poor. Monitoring carried out by the State authorities and by the industrial sector itself is totally inadequate given the scale of the overall problem

In Russia, the national pollution regulation system targets a very limited number of substances and does not include Persistent, Bioaccumulative and Toxic (PBT) substances. Some heavy metals and some phthalates are included in the Baltic Sea Action Plan. Dioxins and PCBs are targeted extremely rarely. Otherwise there is virtually no monitoring of PBT substances and no regulations in place to target these substances. A limited number of samples are analysed for dioxin and PCBs from time to time but without any systematic approach being taken.

Waste water treatment plants (WWTPs) in Russia are regulated by the governmental decree entitled "On the adoption of the rules of water supply and sewerage in the Russian Federation" (Government RF, 1999) This decree gives an exhaustive list of cases where waste water treatment enterprises can disconnect their users from the waste water treatment system. Unfortunately, emissions of prohibited substances or of substances exceeding maximum permissible levels are not specified in the list. As an example if a legally operating industrial entity discharged several tons of mercury, even if it was identified as doing so, the waste water treatment enterprise in question would have no legal rights to stop accepting the highly polluted wastewaters.

The combined sewer systems found in many Russian cities, in common with similar systems elsewhere in Europe, are a historical legacy dating back many decades. In such systems domestic and industrial wastes are combined and treated together. The only solution to prevent contamination of rivers and seas from such sewer systems is to ban hazardous substances from being discharged into them. Elimination of hazardous substances from the system, together with an adequate regime of primary, secondary and tertiary treatment is essential if water quality in the receiving waters is to be maintained to a high standard. This should include adequate pre-treatment of any industrial effluent discharged to the combined system.

The advantages of the *status quo* to industrial enterprises using the municipal wastewater system are clear. The lack of regulatory compulsion to eliminate hazardous substances or to carry out pre-treatment are perhaps the most obvious. In addition, by discharging polluted waste water to municipal sewers the polluter effectively "loses" ownership of the emissions and allowing them to claim that they are a zero discharge company (with regards to discharges to the environment). Accordingly taking out a contract with a municipal waste water treatment facility allows a company to avoid even the current weak state environmental controls currently in operation. For such polluters, even the small list of controlled substances which already exists is not applicable. There are no effective sanctions which can be applied in any case. Municipal treatment systems are generally regional or local monopolies mostly in state ownership. Any financial penalties for regulatory violations, therefore, will simply be a payment from one state owned operation (the WWTP) to another in the form of the Federal Service for Environmental Control and Monitoring.

Unsurprisingly then municipal waste water treatment facilities are the largest water polluters in the country according to the annual reports from the Ministry for Natural Resources and the Environment "The State of the Environment in the Russian Federation in 2009" (see: e.g. MPR&E RF, 2010).

In order to gather more information on this situation, In April-May 2010, Greenpeace collected thirty one samples including river waters, sediments and wastewaters from industrial and WWTP discharges, and the receiving systems. The following rivers were targeted: Syas, Svir`, Sheksna, Koshta, Volga and Moskva. Samples from the Krasny Bor toxic waste landfill drainage canal were also collected. The aim of this work was to expand on a previously conducted investigation on contamination of the River Neva (Labunska, , *et.al*, 2010) and to undertake a preliminary investigation of certain hazardous substances on the waterway between the two "capitals" of the Russian Federation: Moscow and St-Petersburg. This work is not a comprehensive monitoring report but is intended to highlight the need for all stakeholders and authorities to invest in a greatly expanded monitoring program in order to protect human health and the environment and to pave the way for further industrial modernization of the country. There is a great need for such an initiative. As noted previously there is no systematic regulation, monitoring and control of hazardous substances in the Russian Federation. Previous investigations of toxic chemicals in aquatic systems in the Russian Federation have been conducted only occasionally and covered only very limited areas.

Sampling program and description of sampling sites

Leningradskaya Oblast Rivers Syas and Svir`. Krasny Bor toxics waste landfill.

A description of sampling sites and of samples collected in Leningradskaya Oblast is presented in Table 1. Locations of sampling sites are shown in Fig.1. The Syas River flows from the Valdai Hills to the north and into Lake Ladoga. The town of Syasstroy is located at the river mouth. In order to monitor river water quality at the river entry into Ladoga Lake, two sediment samples (RU10003, RU 10005) were taken from either river bank at approximately 1 m depth and a single water sample (RU 10004) was taken from the middle of the river at 1.5 m depth.

The Svir River is located in the north-east of Leningradskaya Oblast, Russia. It flows from Lake Onega west to Lake Ladoga, thus connecting the two largest lakes in Europe. It is the largest river flowing into Lake Ladoga. After Peter the Great connected the Svir with the Neva River with the Ladoga Canal, the river has been part of the Volga-Baltic Waterway. Two sediment samples (RU 10006, RU 10008) were collected from the river close to its entrance to Ladoga Lake from around 1.2 m depth.

Two sampling sites – the Syasskiy pulp and paper mill and junction of Syas river with Ladoga lake were identified for investigation. Syasskiy pulp and paper mill, is the single remaining pulp mill on Ladoga Lake and the River Syas. According to the regional water authority (Nevsko-Ladozhskoe BVU) (NLBVU, 2010), this pulp mill discharges wastes into Volkhovskaya Guba at Ladoga Lake. Before the construction of a pulp and paper mill in the lower part of the river in 1928, up to 10 tons of brown trout were caught annually (BFN, 2008). In 1948 - 57 the yearly catch was 1.8 - 2.4 tones but in later years only 20 - 70 kg per

year were caught (BFN, 2008). Today there are no salmon in the Syas, but non-anadromous brown trout dwell in the upper reaches (BFN, 2008). One water sample (RU 10001) and one solid sample (RU 10002) were taken from a concrete drainage collector which is known as the pulp mill discharge point and which has an aperture for monitoring wastewaters discharged to Ladoga Lake.

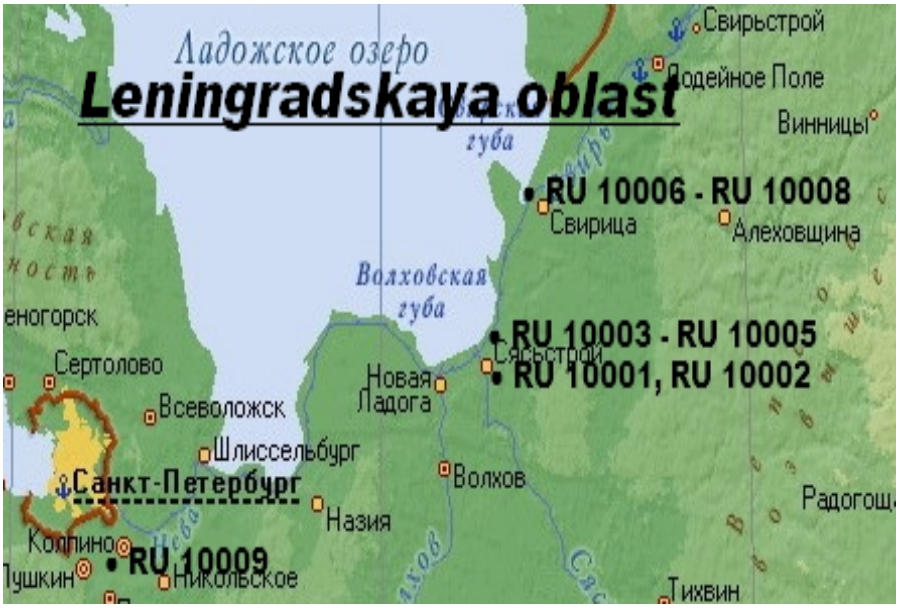

Figure 1. Map of sampling sites location in the Leningradskaya oblast, Russia, 2010.

The Krasny Bor polygon, a toxic waste landfill operated by the St Petersburg Council, is located in the town of Kolpino which is approximately 45 km from St Petersburg. It was established in the late 1960s to "maintain the ecological balance in the region" due to heavy industrialization. The site was chosen based on extensive exploration in the Lomonosov, Pushkin, Vsevolozhsk, Volkhov and Tosno districts. According to the founding justification (Krasny Bor, 2011), Krasny Bor in Leningradskaya Oblast territory was chosen based on:

• favorable geological conditions i.e. thick layers of Cambrian clay as a bottom structure preventing the entry of toxic substances into the groundwater;
• absence of aquifers used for water supply
• no seasonal flooding;
• optimal distance from human settlements and industrial enterprises - sources of waste.

The Krasny Bor polygon was setup to neutralize and then landfill industrial toxic waste originating from industries located in Leningradskaya Oblast and St Petersburg.

The polygon accepts the following types of waste:

• Liquid inorganic waste (such as surface treatment facility galvanic waste);
• Liquid organic waste (resins, solvents, petroleum products, etc.);
• Solid and pasty organic and inorganic waste (sludge from electroplating industry, oil-contaminated soil, etc.);
•Very hazardous wastes containing mercury, cyanide, arsenic, cadmium and other hazardous substances.

Sample Code	Sample Type	Sampling date	Description of the sampling sites
RU 10001	waste water	09.05.10	Syasskiy pulp and paper mill discharge into Staro-Ladozhskiy canal. Concrete drainage collector. Sample was taken from the control hole
RU 10002	solid waste	09.05.10	Syasskiy pulp and paper mill discharge pipe into Ekaterininsky canal. Sample was taken from inside of the pipe
RU 10003	sediment	10.05.10	River Syas. Sample was taken from left river bank at approximately 1.5 m depth
RU 10004	river water	10.05.10	River Syas. Sample was taken in the middle of the river at approximately 1 m depth
RU 10005	sediment	10.05.10	River Syas. Sample was taken from right riverbank at approximately 1 m depth
RU 10006	sediment	10.05.10	River Svir`. Sample was taken from left riverbank at approximately 1.5 m depth
RU 10008	sediment	10.05.10	River Svir`. Sample was taken from right riverbank at approximately 1.2 m depth
RU 10009	surface water	06.06.10	Krasny Bor polygon. Sample was taken from concrete drainage canal which surrounds landfill. Small stream

Table 1. Description of sampling sites and samples collected from Leningradskaya oblast, Russia, 2010.

The treatment of liquid waste basically involves removal of the water component The remaining solid waste fraction is then buried in the clay. Waste compaction by evaporation is carried out in a thermal facility at a temperature of 600°C. Since becoming operational in the early 1970s, the polygon has accumulated approximately 1.7 million m3 of hazardous waste of different classes of toxicity in an area of 50 hectares (HELCOM, 2010). Historically, Krasny Bor has been the primary dumping place for hazardous waste from the NW region and contains high amounts of accumulated toxic chemicals. Complete information on the contents of the polygon ponds is not available; however, it is known to contain at least 100 t of mercury (ACAP, 2005), obsolete pesticides from Leningrad Oblast and six other Russian regions, PCB transformers and capacitors from the region and waste oils from the industry in Leningrad Oblast (HELCOM, 2010).

One water sample (RU 10009) was taken from the concrete drainage canal surrounding landfill. This is a small water stream with a low flow and with a strong chemical smell. The drainage canal enters the River Maly Izhorets, a tributary of the River Izhora, which, in turn is a tributary of the River Neva.

Vologodskaya oblast. Cherepovets, Rivers Koshta, Sheksna and Yagorba

A description of sampling sites and of samples collected in Vologodskaya Oblast is presented in Table 2. Locations of sampling sites are presented in Fig.2. Cherepovets is the largest city in Vologodskaya Oblast, Russia, located on the bank of the Rybinsk Reservoir of the Sheksna River, a tributary of the Volga River.

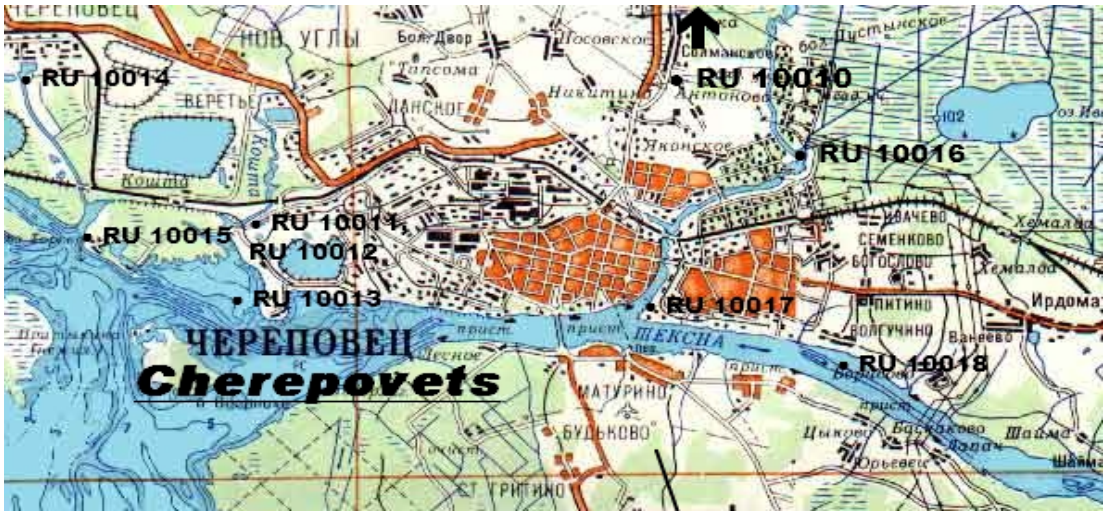

Figure 2. Map of sampling sites location in the Vologodskaya oblast, Russia, 2010.

Sample Code	Sample Type	Sampling date	Description of the sample source
RU 10010	river water	12.05.10	River Koshta, by the road from Cherepovets to Ammofos JSC (also known as road to Novaya Ladoga). Control sample taken from the bridge over the river. Upstream all the industrial sources.
RU 10011	river water	12.05.10	River Koshta, which flows through the Severstal Industrial Estate and in some places directed via pipes inside of several dams. Sample was taken from the pipe before the last dam located about 2 km upstream the junction of River Koshta with River Sheksna.
RU 10012	sediment	12.05.10	River Koshta, same location as for sample RU10011. Sample was taken approximately 50 m from the right hand side of the pipe.
RU 10013	river water	12.05.10	River Koshta at the junction with River Sheksna next to red buoy # 12 from the 30 cm depth.
RU 10014	waste water	12.05.10	Artificial lagoon with green-colored wastewater formed after JSC Ammofos canal and separated by a dam with three pipes discharging into River Koshta. Sample was taken from the pipe with the strongest stream.
RU 10016	river water	12.05.10	River Yagorba, countryside. Upstream control sample was taken after the latest bridge at 30 cm depth.
RU 10017	river water	12.05.10	River Yagorba, farway, in junction with River Koshta, between river ports – passenger and commercial. Sample was taken at 30 cm depth.
RU 10018	river water	12.05.10	River Sheksna. Countryside downstream of Cherepovets. Next to white buoy # 147. Sample was taken from 30 cm depth.

Table 2. Description of sampling sites and samples collected from Vologodskaya oblast, Russia, 2010.

Cherepovets is one of the most significant industrial centers in the north-west of Russia. Frequently the name of the city is associated with the joint stock company "Severstal" whose products are exported to more than fifty countries.

Located at the cross-roads of the major Volga-Baltic waterway, Cherepovets is home to natural resource-consuming industries including Severstal, together with one of the largest iron-and-steel plants in Russia, and as well, some other large factories.

The city began growing rapidly with the construction of the Metallurgical Works in the late 1930s. The first works blast furnace was put into operation in 1955. The first Cherepovets iron was produced in August 1955, and steel followed in May 1958. In February 1959 the first ingot was rolled in a blooming mill and in November of the same year the first hot-rolled plate was produced (Severstal, 2011).

Nowadays the complex production processes of iron and steel making are highly mechanized and automatically operated. The workshops have been modernized according to the latest advances in engineering and technology related to metal production. The joint stock company Severstal is a global exporter of ferrous and non-ferrous metals: iron, steel, hot-rolled plates, cold roll-formed shapes and other products (Severstal, 2011). As a consequence of the presence of this heavy industry, Cherepovets has become one of the most heavily-polluted cities in the world (The Sun, 2010).

To make a preliminary assessment of the impact of local industry on the water of the River Sheksna, samples were collected from its tributaries: the River Koshta and the River Yagorba.

One sample for VOC analysis (RU 10014) was taken from the discharge pipe connecting “green lake” and the industrial canal of JSC “Ammofos” which flows into River Sheksna. The pipe serves as a “valve” to dilute materials into the “lake”. The sample was taken from the pipe with the strongest flowing stream.

For the River Koshta, samples were taken from the JSC Severstal chain of dams. One water sample (RU 10011) was taken before the last dam in the pipe. One sediment sample (RU 10012) also was taken from this sampling site. The dam was located about 2 km upstream of the junction of the River Koshta with the River Sheksna.

A single water sample (RU 10013) was also taken near the junction of River Koshta with River Sheksna. In order to help to identify industrial impacts on the River Koshta one control sample (RU 10010) was taken upstream of the industrial estates.

The River Yagorba, the right-hand tributary of the River Sheksna is classified as a contaminated river according to the Russian national classification system for water bodies (MPR&E RF, 2010). In the upper part of the river, contaminants mainly arise from the agricultural sector.

The aim of the sampling on River Yagorba was to attempt a preliminary estimate of the scale of the river pollution resulting from the industrial activities carried out in the city of Cherepovets. Accordingly, one control sample (RU 10016) was collected from the upper part of the river, at a rural location upstream of Cherepovets and a second sample (RU 10017) was collected at in the unction with the River Koshta between the passenger and commercial river ports located in Cherepovets.

The River Sheksna is the left-hand tributary of the River Volga. It originates from the Lake Beloye and joins the northern part of the Rybinsk Reservoir of the Volga near the city of Cherepovets. Currently, it has a length of 139 kilometers. Originally it was some 400 kilometers long, and joined the Volga at Rybinsk, but the lower part was flooded, and became a part of the Rybinsk Reservoir. The River Sheksna is a part of the Volga-Baltic Waterway. One control sample (RU 10018) was taken from a rural lcation upstream of the city of Cherepovets close to white buoy # 147 at 30 cm depth.

Yaroslavl Oblast. Yaroslavl, Rybinsk and River Volga

A description of sampling sites and of samples collected in Yaroslavl Oblast is presented in Table 3. The locations of sampling site are presented in Fig.3 and Fig.4. Yaroslavl is located 250 kilometers north-east of Moscow at the confluence of the Volga and the Kotorosl Rivers. One of the aims of the current study was to identify the impact from large waste water treatment facilities of combine sewage discharges on the receiving water bodies. Yaroslavl Wastewater Treatment Plant (YWWTP) was chosen as the site for this research.

Sample Code	Sample Type	Sampling date	Description of the sample source
RU 10019	waste water	14.05.10	Wastewater discharge from main Yaroslavl WWTP to River Volga via two canals. Each canal more than 1 km long. This sample has been taken from the first canal if to count from the city.
RU 10020	waste water	30.05.10	Repeat of sample Nr. RU 10019.
RU 10021	waste water	14.05.10	Wastewater discharge from main Yaroslavl WWTP to River Volga via two canals. Each canal more than 1 km long. This sample has been taken from the second canal if to count from the city.
RU 10022	Sediment	30.05.10	River Volga about 100m downstream of main Yaroslavl WWTP. Sample taken at 1.5 m depth.
RU 10023	waste water	28.05.10	Unidentified discharge pipe to River Volga strait after the Rybinsk City stadium. Sample taken from pipe.
RU 10024	sediment	28.05.10	Same location as RU10023. Sample taken from River Volga next to discharge pipe.
RU 10025	waste water	28.05.10	Unidentified wastewater discharge to River Volga about 100 m downstream of Polyot Cultural Centre, Rybinsk. Sample taken from pipe.
RU 10026	sediment	28.05.10	Sample taken from River Volga about 50 m downstream from sample RU10025.

Table 3. Description of sampling sites and samples collected in the city of Yaroslavl and the city of Rybinsk, Russia, 2010.

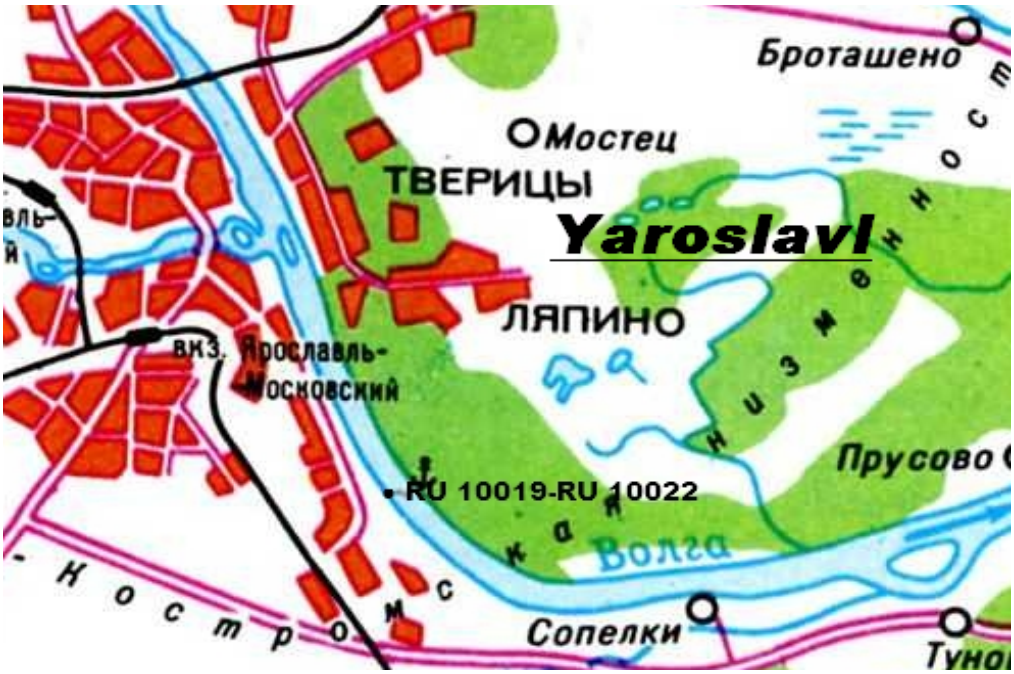

Figure 3. Map of sampling site location in the City of Yaroslavl Russia, 2010.

The capacity of the YWWTP is about 415,000 m^3/day (JSC Yaroslavlvodokanal 2011). YWWTP discharges its wastewaters via two concrete canals from "new" and "old" parts of the plant. Samples were taken from both outlets. Two duplicate samples were taken from the first outlet: RU 10019 was taken on 14.05.2010 and duplicate sample RU 10020 was taken on 30.05.2010. From the second discharge, a single sample (RU 10021) was taken on 14.05.2010. One sediment sample (RU 10022) was collected from a small embayment of the River Volga approximately 100 m downstream of the YWWTP discharge point.

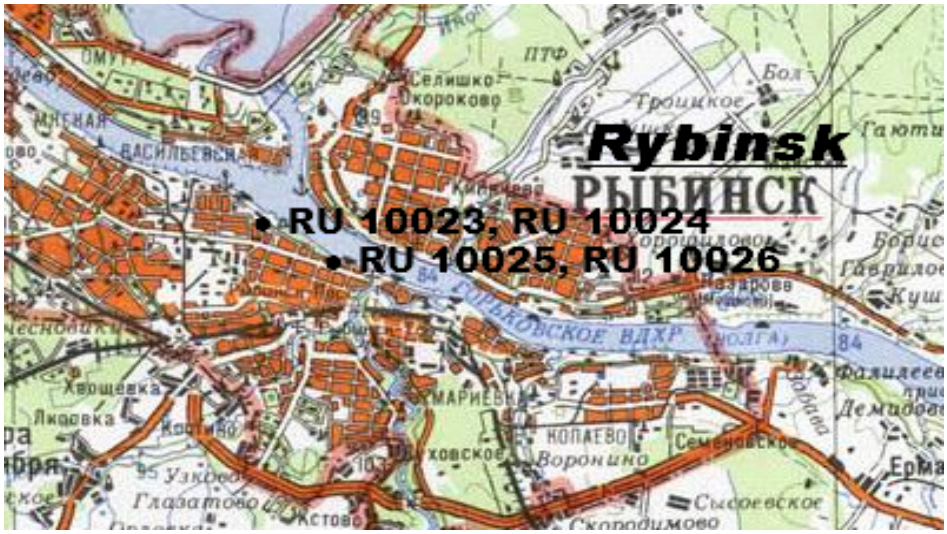

Figure 4. Map of sampling sites location in the City of Rybinsk, Russia, 2010.

Rybinsk is the second largest city in the Yaroslavl Oblast region of Russia. It is located at the confluence of the Volga and Sheksna Rivers. One unidentified wastewater discharge to

the Volga river was located downstream of the city stadium. One water sample (RU 10023) from this discharge and one sediment sample (RU 10024) from close by the discharge were collected. A second unidentified wastewater discharge to River Volga was located 100 meters downstream of the Polyot Cultural Centre. Wastewater (RU 10025) and sediment (RU 10026) samples were collected at this location.

Moscow and River Moskva

A description of sampling sites and of samples collected in Moscow Oblast are presented in Table 4.The locations of sampling site are presented in Fig.4. The Moskva River flows through the Moscow Oblast and Smolensk Oblast areas of Russia, and is a tributary of the Oka River. The length of the river is 503 km. The area of its drainage basin is 17,600 km².

Sample Code	Sample Type	Sampling date	Description of the sample source
RU 10027	waste water	24.05.10	Kuriyanovskie WWTP, underwater discharge to River Moskva via several pipes. Sample was taken from River Moskva at the place with visible stream of underwater discharge at a depth of about 0.5 m. Fecalia were observed in discharge stream.
RU 10028	sediment	24.05.10	River Moskva 500 m upstream of Kuriyanovskie WWTP. Sample taken from a left riverbank in a small bay at a depth about 1.6 m.
RU 10029	sediment	24.05.10	Right bank of River Moskva opposite to Kuriyanovskie WWTP. Sample taken from small bay near Kolomenskiy park at depth of about 1.6 m. It was observed that flow of WWTP underwater discharge goes to this bay.
RU 10030	sediment	24.05.10	Sample taken from River Moskva 500 m upstream of Kuriyanovskie WWTP, from the right riverbank at the depth about 0.7 m
RU 10031	river water	24.05.10	Sample taken from River Moskva 500 m downstream of Kuriyanovskie WWTP from fairway at the depth about 0.5 m
RU 10032	sediment	24.05.10	Sample taken from River Moskva 500 m downstream Kuriyanovskie WWTP, left riverbank at the depth about 1.5 m
RU 10033	sediment	24.05.10	Sample taken from left bank of River Moskva after Moscow circle road bridge at the depth about 1.5 m

Table 4. Description of sampling sites and samples collected in the city of Moscow, Russia, 2010.

Kuryanovskaya secondary biological treatment station is located in the south east of Moscow. Total capacity 3.125 million cubic meters per day. This WWTP is considered to be one of the largest WWTP in Europe (MSUE Mosvodokanal 2011) if not the largest. Treated waters are discharged directly to the Moskva River via a long canal with a dam at the end. Several underwater pipes pump waste waters through the dam. In order to identify impacts from the WWTP, samples were collected from the treated water discharge of Kuryanovskaya secondary biological treatment station (RU 10027). A sample was taken from the Moskva River at the location of the visible of underwater discharge at a depth of about 0.5 m.

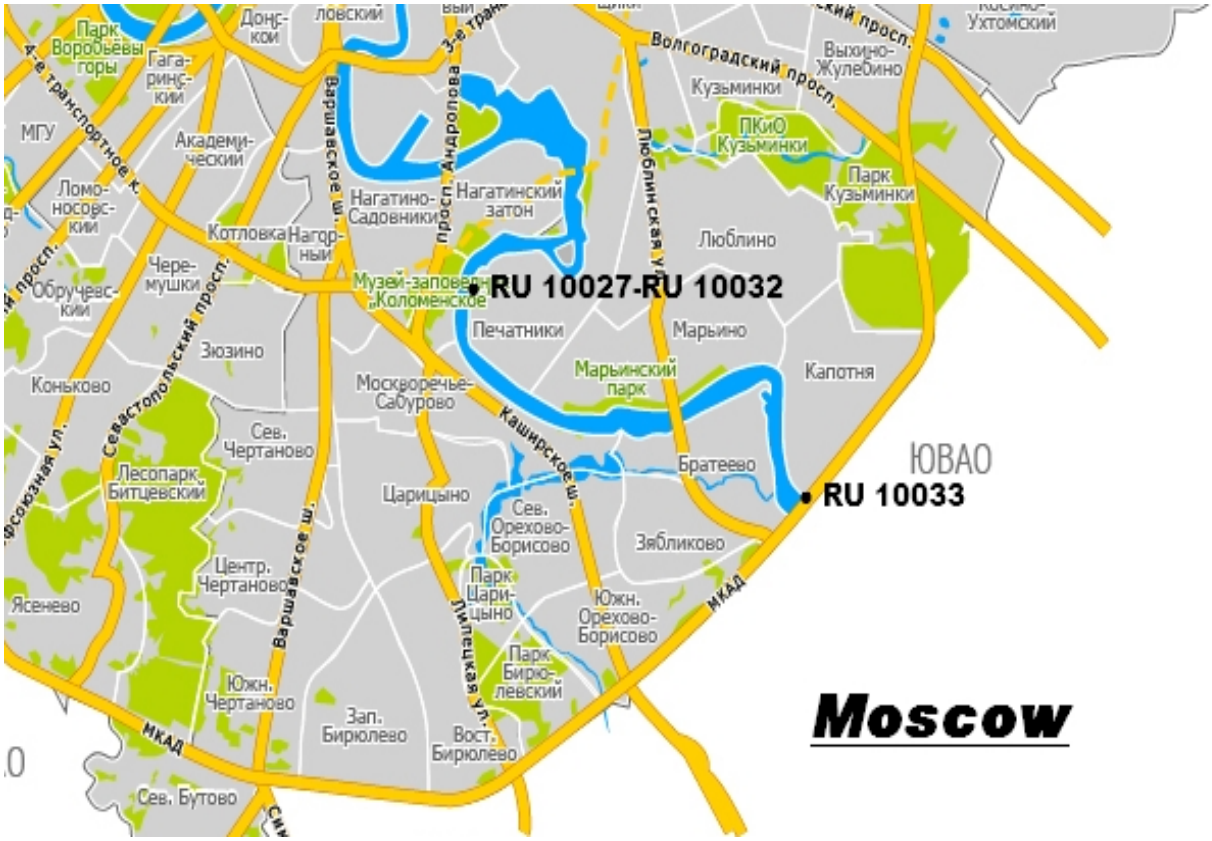

Figure 5. Map of sampling sites location in the City of Moscow, Russia, 2010.

Sediment samples from the Moskva River were collected upstream (RU 10028, RU 10029, RU 10030) and downstream (RU 10031, RU 10032) of the Kuriyanovskie WWTP .

For a preliminary assessment of the City of Moscow impact on the Moscow River, one sediment sample (RU 10033) was taken from the left bank of the river downstream of the Moscow circle road bridge which is officially recognized as the city boundary downstream of the city of Moscow.

Results and discussion

All samples considered in this study have been subject to quantitative analysis for heavy metals and qualitative organic screening analyses. Additionally, seven samples of wastewater and one sample of surface water were quantitatively analysed for the presence of volatile organic compounds (VOCs). Results for VOCs analysis is presented in Table 5, for heavy metals and organic screening analyses – in Tables 6 – 12. The discussion of results is presented below accordingly to the geographical location of sampling sites.

Compound	LOQ, µg/l	RU 10001	RU 10009	RU 10014	RU 10019	RU 10021	RU 10023	RU 10025	RU 10027
Vinyl chloride	1	n/d	2	n/d	n/d	n/d	n/d	n/d	n/d
Methane, dichloro-	1	n/d	35	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, 1,2-dichloro-, trans-	2	n/d	<2	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, 1,2-dichloro-, cis-	1	n/d	19	n/d	n/d	n/d	n/d	n/d	n/d
Chloroform	1	25	19	n/d	3	<1	13	8	n/d
Ethane, 1,1,1-trichloro-	1	n/d	1	n/d	n/d	n/d	n/d	n/d	n/d
Benzene	1	n/d	7	n/d	n/d	n/d	n/d	n/d	n/d
Ethane, 1,2-dichloro-	1	<1	8	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, trichloro-	1	n/d	12	n/d	n/d	n/d	n/d	n/d	n/d
Toluene	1	n/d	49	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, tetrachloro-	1	n/d	8	n/d	n/d	<1	n/d	n/d	1
Benzene, chloro-	2	n/d	3	n/d	n/d	n/d	n/d	n/d	n/d
m- & p-Xylene	2	n/d	23	n/d	n/d	n/d	n/d	n/d	n/d
o-Xylene	2	n/d	16	n/d	n/d	n/d	n/d	n/d	n/d
Toluene, 2-chloro-	2	n/d	<2	n/d	n/d	n/d	n/d	n/d	n/d

Table 5. Concentrations of volatile organic compounds (VOC), in µg/l, in wastewater samples collected from selected discharges including Syas pulp and paper mill (RU10001), drainage canal around Krasny Bor toxic waste dump (RU10009), canal from JSC Ammofos (RU10014), Yaroslavl WWTP (RU10019,RU10021, and RU10023), Polyot cultural house by River Volga, Yaroslavl (RU10025), and Kuriyanovskie WWTP (RU10027). Russia, 2010. LOQ - limit of quantification, n/d - not detected.

Leningradskaya oblast. Rivers Syas and Svir`. Krasny Bor toxics waste landfill.

Syasskiy pulp and paper mill

Two samples were collected in the vicinity of the Syasskiy pulp and paper mill: treated wastewater sample RU 10001 and solid waste RU10002 from inside the discharge pipe. The water sample was not significantly contaminated with any of the quantified metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. Organic screen analysis revealed the presence of 149 organic compounds in this sample indicating the complexity of wastewaters originating from this plant. Typically for organic chemicals in wastes and environmental samples, only a relatively small proportion of the organic compounds isolated could be identified with any reliability. 47 organic compounds (32%) have been reliably identified in sample RU10001 (see Tables 6 & 7). The majority of these organic compounds are frequently found in wastewaters from pulp and paper mills including phenolic acids and alkylated and chlorinated derivatives of phenol; guaiacol and its alkylated and chlorinated derivatives; terpenes and derivatives; aldehydes, alcohols and ketones (Olaniran & Igbinosa 2011, Lacorte *et al.* 2003, RTP 1994, Kukkonen *et al.* 1996). The presence of chlorinated phenols and guaiacols in the wastewater from Syasskiy pulp and paper mill indicates the usage of chlorine or other chloro-containing agents during pulp bleaching processes (Stringer & Johnston 2001). It is well known that chlorinated phenolic compounds are among the main chemicals responsible for the toxicity of pulp and paper mill effluents and may be mutagenic and/or carcinogenic (Ali & Sreekrishnan 2001). Vanillin, the major degradation product of natural lignin and humic compounds, and several of its derivatives were also detected in sample RU10001. Other compounds derived from the sample included:

- The plasticizers: dibutyl phthalate and tributyl phosphate;
- The phosphorous-based flame retardant: tris(2-butoxyethyl) phosphate;
- i**socyanatocyclohexane** which is used in manufacture of foams, rubber, paints and varnishes.

Sample RU10001 also contained two VOCs: chloroform at 25 µg/l and trace levels of 1,2-dichloroethane (<1 µg/l) – see Table 5. These substances also indicate the use of chlorine or chlorine based bleaching agents in the mill. To regulate the water quality of rivers, specifically in fishing areas, the Russian Federation has set Maximum Permissible Levels (MPL) for hazardous substances in fresh water courses (FAF RF 2010), which are presented in Table 8. The concentration of chloroform in sample RU10001 exceeded the MPL for this chemical by a factor of five times. Chloroform is considered to be the major chlorinated alkane produced during pulp bleaching processes using gaseous chlorine (RTP 1994).

Sample	**RU10001**	**RU10002**	**RU10003**	**RU10004**	**RU10005**	**RU10006**	**RU10008**	**RU10009**
Type	**waste water**	**solid waste**	**sediment**	**river water**	**sediment**	**sediment**	**sediment**	**surface water**
Location	Syas P+P drainage collector	Syas P+P discharg e pipe	River Syas, left bank	River Syas, 1m depth	River Syas, right bank	River Svir', left bank	River Svir', in the middle	Krasny Bor landfill, drainage canal
METAL	µg/l	mg/kg	mg/kg	µg/l	mg/kg	mg/kg	mg/kg	µg/l
Antimony	<50	<20	<20	<50	<20	<20	<20	<50
Arsenic	<50	<20	<20	<50	<20	<20	<20	<50
Barium	89	255	187	33	100	94	17	47
Cadmium	<5	<1	<1	<5	<1	<1	<1	<5
Chromium	<20	85	43	<20	20	30	6	30
Chromium (VI)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Cobalt	<20	8	17	<20	10	8	3	<20
Copper	<20	63	21	<20	17	11	<2	<20
Lead	<50	7	12	<50	7	6	2	<50
Manganese	454	424	1400	81	627	330	68	402
Mercury	<2	<0.5	<0.5	<2	<0.5	<0.5	<0.5	<2
Nickel	<20	30	24	<20	11	15	4	38
Selenium	<200	<30	<30	<200	<30	<30	<30	<200
Vanadium	<20	17	47	<20	22	33	8	<20
Zinc	49	24	112	<10	87	49	16	120
No. of organic compounds isolated	149	4	12	1	3	1	none	137
No. of reliably identified compounds (% of total)	47(32%)	2(50%)	5(40%)	none	none	none	none	48(35%)
Aliphatic hydrocarbons	nd	2	3	nd	nd	nd	nd	nd
PAH derivatives	nd	nd	1	nd	nd	nd	nd	nd
Ketones	nd	nd	1	nd	nd	nd	nd	nd
Others	see Table 7	nd	nd	nd	nd	nd	nd	See Table 9

Table 6. Organic compounds identified, and concentrations of metals, in samples of wastewater and solid waste associated with Syas pulp and paper mill, river water and river sediments collected from River Syas and Svir, and surface water from drainage canal around Krasny Bor toxic waste landfill, Leningradskaya Oblast, Russia,

2010. Concentrations of metals in water samples are reported in μg/l as total concentrations in the whole (unfiltered) sample. Concentrations of metals in sediments are reported as mg/kg dry weight; nd – not detected.

Name	RU10001
Volatile organic compounds (see Table 5)	(2)
Chlorinated phenols	4
Phosphoric acid esters	2
Phthalate esters	1
Alkylated phenols *(other than nonyl- and octylphenols)*	3
Phenolic aldehydes (vanillin)	1
Guaiacol (methoxyphenol) and alkylated derivatives	5
Chlorinated guaiacols	1
Terpenes and derivatives	8
Aliphatic/aromatic ketones and derivatives	7
Alkylated benzenes	1
Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	1
Benzenepropanoic acid, 4-hydroxy-3-methoxy-	1
Benzoic acid, 4-hydroxy-3-methoxy- (Vanillic acid)	1
Alcohols	2
Homovanillic acid and derivatives	2
Cyclohexane, isocyanato-	1
Ethanol, 2-(2-butoxyethoxy)-, acetate	1
trans-Z-.alpha.-Bisabolene epoxide	1
Z,E-3,13-Octadecadien-1-ol acetate	1
Spiro[4.5]dec-8-en-7-ol, 4,8-dimethyl-1-(1-methylethyl)-	1

Table 7. List of organic compounds reliably identified in the wastewater sample RU10001 collected from Syas pulp and paper mill discharge into Staro-Ladozhskiy canal, Lerningradskaya Oblast, Russia, 2010. (#) - signifies number of compounds identified at trace levels using a selective SIM method.

The concentration of copper in the solid waste (RU10002) was slightly higher than levels typically found in uncontaminated freshwater sediments, which are usually below 50 mg/kg (ATSDR 2004). Only four organic compounds were isolated from this sample and two of them were reliably identified as linear aliphatic hydrocarbons which could be of natural origin.

Thus, the Syasskiy pulp and paper mill plant acts as a point source of a diverse range of toxic organic chemicals. These include chlorinated compounds, which are probably derived from bleaching processes and which are discharged with wastewater directly to the Volkhovskaya Guba of Ladoga Lake. It is long known that pulp and paper manufacture has the potential to seriously impact environmental quality and hence the health of both human and wider ecosystems (Martel *et al*. 1994, Ali & Sreekrishnan 2001, Orrego *et al.* 2011, Ritchlin & Johnston1998, Thompson *et al*. 2001). Hence, in order to eliminate these compounds it is necessary to convert to a totally chlorine-free (TCF) pulp bleaching process which eliminates the generation of chlorinated compounds in associated wastes (Johnston *et al.* 1997). Moreover, introduction of a closed-loop production configuration will prevent the discharge of contaminants to the environment (Thompson *et al.* 2001, Zhang *et al.* 2009, Johnston *et al.* 1997).

Compound	MPL, µg/l
Vinyl chloride	Absence (0,008 µg/l as a reference point)
1,1,1,2-tetrachloroethane	10
1,1,2,2-tetrachloroethane	50
1,2-dichloroethane	100
Chloroform	5
toluene	500
Chlorobenzene	1
Benzene	500
Orto-Xylene	50
Para-Xylene	5

Table 8. Maximum Permissible Levels (MPL) of hazardous substances in water of fisheries water objects (FAF RF 2010)

Rivers Syas and Svir

The results for environmental samples analyses from Rivers Syas and Svir are presented in Table 6. The river water sample (RU10004) was not significantly contaminated with any of the quantified metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. No organic compounds were isolated from this sample.

The concentrations of the quantified metals in all sediment samples from River Syas (RU 10003, RU 10005) and River Svir (RU 10006, RU 10008) were within the typical ranges reported for these metals in uncontaminated river sediments. Only one of these samples (RU10003) collected from the left bank of River Syas contained organic compounds. Among 12 compounds isolated from this sample five were reliably identified as dimethylheptadienone, alkylated phenanthrene, together with two linear aliphatic hydrocarbons.

Drainage canal around Krasny Bor landfill

One sample of surface water was collected from the canal around the Krasny Bor landfill, which discharges into the River Maly Izhorets. This sample contained nickel at a concentration of 39 µg/l. This is slightly higher than levels found in uncontaminated surface waters, which are typically below 20 µg/l (ATSDR 2005a). Concentrations of other metals considered in this study were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters.

In contrast, this sample contained a high load of organic compounds the majority of which undoubtedly originated from the landfill. 137 organic compounds were isolated and 48 of those (35%) were reliably identified (see Table 9). Many of these compounds are known to be toxic and persistent chemicals including chlorinated benzenes and chlorinated phenols, biocides (pesticides and herbicides), alkylated and chlorinated esters of phosphoric acid, and the nonionic surfactant Surfynol 104H. Four pharmaceutical chemicals were also detected in the sample.

Name	RU10009
Volatile organic compounds (see Table 5)	4(11)
Chlorinated phenols	1(3)
Phosphoric acid esters	6
Trichlorinated benzenes	(2)
Pesticides and herbicides (Triadimefon, Acetochlor, Oxydixyl, HCH isomers, Atrazine, Prometryn, Ridomil, Diphenylamid, Eptam, Pirimicarb)	11
Pharmaceuticals (caffeine, carbamazepine, pentoxifylline, phenobarbital)	4
Surfynol 104H	1
N-ethyl-1,3-dithioisoindoline	1
Phenethanamine, N-acetyl-4-cyano-	1
Pyridine derivatives	2
Quinoxaline, 2,3-dimethyl-	1

Table 9. List of organic compounds reliably identified in the surface water sample RU10009 collected from a drainage canal around Krasny Bor toxic waste dump, Lerningradskaya Oblast, Russia, 2010. (#) - signifies number of compounds identified at trace levels using a selective SIM method.

Moreover, sixteen toxic VOCs, eleven of which were chlorinated hydrocarbons, have been detected in this sample despite the fact that sample was collected from an open watercourse (in which evaporation processes are likely to be significant in reducing the concentrations of such chemicals). Non-chlorinated VOCs identified in this sample were benzene, toluene and three isomers of xylene (BTEX) The list of VOCs detected in this sample and their concentrations are presented in Table 5. According to the Russian Federation regulation (FAF RF 2010), vinyl chloride should not be present in river waters (with the exception at almost undetectable level of 0.008 μg/l as a reference point), however, sample RU10009 contained 2 μg/l of this toxic chemical. The levels of chloroform and chlorobenzene in this sample were 3.8 and 3 times the MPL respectively. The sum of two *para*-xylenes detected in the sample was 23 μg/l, which is approximately two times the MPL for each isomer separately. Benzene, toluene and *ortho*-xylene were detected at levels below MPL. However, there are no MPLs in place for other toxic chlorinated VOCs quantified in this sample, namely: dichloromethane, *trans*- and *cis*- isomers of 1,2-dichloroethene, tri- and tetrachloroethene, 1,1,1-trichloroethane, 1,2-dichloroethane, and 2-chlorotoluene.

As noted above in the sample description section, water from the Krasny Bor canal finally enters River Maly Izhorets, a tributary of the River Izhora, which is also a tributary of the River Neva. The presence of mobile compounds (e.g. compounds in a soluble form) in the Krasny Bor drainage canal such as chlorinated benzenes, chlorinated phenols, together with a wide range of biocides and pharmaceuticals is very alarming. Taking into account that water from the canal directly enters natural water courses, it is reasonable to deduce that the landfill could act as a source of toxic organic compounds to the surrounding environment through direct run-off of leachate and mobilization of sediments or by migration through the solid wastes, soils and sediments in the landfill. It is also important to note that the site could act as a source of such toxic compounds as a result of their re-volatilisation to, and distribution through, the atmosphere. It was not possible, however, to determine from this limited study any information regarding the actual extent of contamination around the canal or the Krasny Bor landfill as a whole

Vologodskaya oblast. Cherepovets, Rivers Koshta, Sheksna and Yagorba

River Koshta

The results from analyses of samples collected from Vologodskaya Oblast are presented in Table 10. The control river water sample RU10010, which was collected in the upper part of the River Koshta, was not significantly contaminated with either organic compounds or with any of the quantified metals. The only organic compound which was reliably identified in this sample was tributyl ester of phosphoric acid (TBP). This has various uses including as a solvent, as a plasticiser, as a metal extractant, as a flame retardant, or as an antifoaming agent. It is unclear what the source of this chemical in sample RU10010 could be. Metal concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters.

Two samples were collected in the lower part of the River Koshta after its travel through the Severstal Industrial Estate, by the last dam where river is directed through a pipe. The water sample RU10011collected from the pipe contained an elevated zinc concentration at 230 μg/l which is uncommon for uncontaminated fresh water which usually contains <50 ug/l (USPHS 1997). The sediment sample RU10012 collected close to the location of the river water sample RU10011 contained a particularly high level of zinc (3660 mg/kg), far above levels typically reported in uncontaminated freshwater sediments, which are commonly below 100 mg/kg (ATSDR 2005b). This may indicate that the high zinc concentration in the sediment is a result of the ongoing discharge of water containing high levels of zinc *via* this pipe/river. However, it cannot be discounted that the level of zinc in the water sample was due to re-suspension of zinc from sediment within the pipe/river back into water flowing through it. Sediment sample RU10012 also contained high levels of cadmium, copper and lead, and also, though to a lesser extent chromium and nickel. Levels in uncontaminated freshwater sediments are commonly reported to be below 2 mg/kg (cadmium), 50 mg/kg (copper) and 30 mg/kg (lead), respectively (ATSDR 2008, ATSDR 2004, ATSDR 2007a). These data indicate that the accumulation of metals within the sediment has taken place due to their presence in waters that have been discharged to the River Koshta within the Industrial Estate. Other than for zinc, the metals present at high levels in the sediment sample RU10012 were not detected in the water sample RU10011, suggesting that their accumulation in the sediment is due either to historic discharges, or possibly due to ongoing discharge of waters with considerable variation in composition such that the water contains high levels of these metals at other times.

Organic contaminants were detected only in the sediment sample from this site (RU10012), but not in the river sample RU10011. Those detected, were mainly representatives of PAHs (nineteen compounds), aliphatic hydrocarbons (17 compounds), and oxygenated aromatic hydrocarbons (benzofuran and its derivative; and 2-methylphenol). PAHs are well known persistent environmental contaminants which are toxic to humans, animals and aquatic life. The presence of PAHs in this sediment sample most likely reflects the input from the Severstal Industrial Estate which has a variety of industries including iron/steel and metallurgy. Such industrial activities are characterized by high emission of PAHs to the environment (Li *et al.* 2011).

River water sample RU10013 collected at the junction of the River Koshta and the River Sheksna did not contain any organic compounds reliably identified and also was not significantly contaminated with any of the quantified metals.

Ammofos waste lagoon

A single sample of water RU 10014 was collected from the JSC Ammofos artificial waste lagoon separated by a dam with three pipes discharging into the River Koshta. A limited number of organic compounds were isolated from this sample with only two being reliably identified as aliphatic hydrocarbons. However, this sample contained a reasonably high arsenic concentration (total 116 µg/l, dissolved 90 µg/l). Arsenic may be released to the environment from natural sources; however, releases from anthropogenic sources far exceed those from natural sources. Anthropogenic sources of arsenic include nonferrous metal mining and smelting, pesticide application, coal combustion, wood combustion, and waste incineration. Most anthropogenic releases of arsenic are to land or soil are primarily in the form of pesticides or solid wastes. However, substantial amounts are also released to air and water. Concentrations in uncontaminated water are usually <10 µg/l although higher levels may occur near natural mineral deposits or anthropogenic sources (ATSDR 2007b). According to the JSC Ammofos web-site information (Ammofos 2011), this plant produces a range of phosphorous-containing fertilizers, concentrates from apatite-nephelinic ore, animal food with potassium phosphate, and range of commodity chemicals such as ammonia, nitric and sulphuric acids, and sodium silicofluoride. Thus, the source of arsenic in the waters discharging from the lagoon into the River Koshta is unclear and needs to be further investigated.

Sample	**RU10010**	**RU10011**	**RU10012**	**RU10013**	**RU10014**	**RU10016**	**RU10017**	**RU10018**
Type	**river water**	**river water**	**sediment**	**river water**	**waste water**	**river water**	**river water**	**river water**
Location								
METAL	µg/l	µg/l	mg/kg	µg/l	µg/l	µg/l	µg/l	µg/l
Antimony	<50	<50	<20	<50	<50	<50	<50	<50
Arsenic	<50	<50	<20	<50	116	<50	<50	<50
Barium	46	49	182	25	66	21	15	16
Cadmium	<5	<5	12	<5	<5	<5	<5	<5
Chromium	<20	<20	188	<20	<20	<20	<20	<20
Chromium (VI)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Cobalt	<20	<20	28	<20	<20	<20	<20	<20
Copper	<20	<20	186	<20	<20	<20	<20	<20
Lead	<50	<50	217	<50	<50	<50	<50	<50
Manganese	180	187	1680	67	573	59	35	33
Mercury	<2	<2	<0.5	<2	<2	<2	<2	<2
Nickel	<20	<20	95	<20	<20	<20	<20	<20
Selenium	<200	<200	<30	<200	<200	<200	<200	<200
Vanadium	<20	<20	124	<20	<20	<20	<20	<20
Zinc	12	203	3660	41	17	30	<10	<10
No. of organic compounds isolated	3	7	62	24	7	13	8	4
No. of reliably identified compounds (% of total)	1(33%)	none	42(68%)	none	2(29%)	10(77%)	4(50%)	none
Phosphoric acid esters	1	nd	nd	nd	nd	nd	nd	nd
PAH derivatives	nd	nd	19	nd	nd	nd	nd	nd

Other aromatic hydrocarbons	nd	nd	6	nd	nd	nd	nd	nd
Fatty acids and its esters	nd	nd	nd	nd	nd	4	nd	nd
Alcohols	nd	nd	nd	nd	nd	nd	2	nd
Aliphatic hydrocarbons	nd	nd	17	nd	2	6	2	nd

Table 10. Organic compounds identified, and concentrations of metals, in samples of wastewater, river water and river sediments collected from River Koshta and River Yagorba, industrial area of Cherepovets city, Russia, 2010. Concentrations of metals in water samples are reported in µg/l as total concentrations in the whole (unfiltered) sample. Concentrations of metals in sediments are reported as mg/kg dry weight; nd – not detected;

Rivers Yagorba and Sheksna

These three river water samples RU10016-18 were not significantly contaminated with any of the quantified metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. Organic compounds were detected in a limited number only in samples from the River Yagorba RU10016 and RU10017, which were mainly representatives of aliphatic hydrocarbons and fatty acids that might be of natural origin. No organic compounds were detected in the sample RU10018.

Yaroslavl Oblast. Yaroslavl, Rybinsk and River Volga

Yaroslavl WWTP

Analytical results for samples collected in Yarislavl Oblast are presented in Table 11. Four samples were collected in the vicinity of the main Yaroslavl WWTP: three wastewater samples of which two RU10019 and RU10020 were collected from the same discharge canal on a different date and RU10021 collected from the second discharge canal on the same day as sample RU10119. A single sample of sediment RU10022 was taken from River Volga about 100m downstream of main Yaroslavl WWTP discharge. None of the wastewater and sediment samples RU10019-RU10022 were significantly contaminated with any of the quantified metals.

The results for organic compounds screening of all three wastewater samples showed a similar pattern of pollutants. The number of organic compounds isolated from each sample was moderately high at 44, 68 and 67 for samples RU10019, RU10020 and RU10021 respectively. From those isolated, a proportion of compounds were reliably identified: 11 compounds for sample RU10019 and 10 compounds each for RU10020 and RU10021. All three wastewater samples contained the following compounds:

- Galaxolide, a polycyclic synthetic musk;
- 2,4,7,9-Tetramethyl-5-decyn-4,7-diol, also known as Surfynol 104, used as an industrial defoaming, nonionic surfactant;
- the chlorinated phosphorous flame retardant tri(2-chloroethyl) phosphate;
- the chlorinated phosphorous flame retardant tris-(2-chloroisopropyl) phosphate (trade name Fyrol PCF);
- the insect repellent Benzamide, N,N-diethyl-3-methyl-, also known as DEET.

Two samples RU10019 and RU10021 collected from separate discharge canals on the same day also contained:

- the phosphate ester flame retardant tri(2-butoxyethyl) phosphate (trade name Kronitex KP-140);
- Chloroform at trace levels (3 μg/l and <1 μg/l respectively), a disinfection byproduct;
- Phenobarbital, a chemical that belongs to a group of medicines called barbiturates;
- the phenolic antioxidant used for long-term thermal stabilization 2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (trade name Irganox 1076).

Both samples RU10019 and RU10020 collected from the same canal, but on different days (16 days between sampling) also contained 2,2,6,6-tetramethyl-4-piperidinone, also known as triacetonamine, an intermediate for the synthesis of pharmaceutical products, pesticides and photostabilizers for polymers. Also, several compounds were detected in only one of the three samples reflecting periodic variations in the quality of the final treated effluent being discharged (see Table 11). However, it is clearly evident that similar types of pollutants, some of which are toxic and/or persistent, are continuously discharged from this facility. This analysis revealed that treatment of wastewater on the Yaroslavl WWTP is not capable of preventing these pollutants from being discharged to the River Volga; therefore this facility is acting as a significant point source of organic pollutants to the environment downstream. As evidence for this, organic analysis of the sediment sample RU10022 collected from River Volga 100m downstream of Yaroslavl WWTP, has shown the presence of one of the contaminants detected in the wastewater samples RU10019 and RU10021 - the phenolic antioxidant Irganox 1076. Furthermore, sludges generated by the treatment plant are likely to contain a significant proportion of the contaminants that are most resistant to degradation. This may lead to a much wider spread of contamination as a result of subsequent disposal of treatment plant sludges.

Rybinsk city and River Volga

Four samples were collected in the city of Rybinsk: wastewater samples from two unidentified discharges (RU10023 and RU10025) and two associated sediments from the River Volga (RU10024 and RU10026).

Water discharged via pipe to River Volga immediately downstream of the Rybinsk City stadium (sample RU 10023) contained nickel at a concentration (37μg/l) slightly higher than levels found in uncontaminated surface waters, which are typically below 20 μg/l (ATSDR 2005a). Four organic compounds were reliably identified in this sample including:

- Phosphoric acid, tributyl ester (TBP), used as a solvent, as a plasticiser, as a metal extractant, as a flame retardant, and as an antifoaming agent;
- Tri(2-chloroethyl) phosphate, the chlorinated phosphorous flame retardant;
- Chloroform at a concentration of 13 μg/l.

The level of chloroform detected in this sample was more than twice the MPL for freshwaters used for fishing (FAF RF 2010). The sediment sample RU 10024 collected next to this discharge had no organic compounds reliably detected and concentrations of the quantified metals were within the typical ranges reported for these metals in uncontaminated river sediments.

Sample	**RU10019**	**RU10020**	**RU10021**	**RU10022**	**RU10023**	**RU10024**	**RU10025**	**RU10026**
Type	**waste water**	**waste water**	**waste water**	**sediment**	**waste water**	**sediment**	**waste water**	**sediment**
Location								
METAL	µg/l	µg/l	µg/l	mg/kg	µg/l	mg/kg	µg/l	mg/kg
Antimony	<50	<50	<50	<20	<50	<20	<50	<20
Arsenic	<50	<50	<50	<20	<50	<20	<50	<20
Barium	27	17	19	70	80	40	80	55
Cadmium	<5	<5	<5	<1	<5	<1	<5	<1
Chromium	49	<20	<20	59	<20	23	<20	53
Chromium (VI)	-	-	-	-	-	-	-	-
Cobalt	<20	<20	<20	5	<20	8	<20	19
Copper	<20	<20	<20	11	<20	22	<20	28
Lead	<50	<50	<50	6	<50	11	<50	11
Manganese	52	24	33	218	246	478	81	301
Mercury	<2	<2	<2	<0.5	<2	<0.5	<2	<0.5
Nickel	<20	<20	<20	10	36	38	<20	134
Selenium	<200	<200	<200	<30	<200	<30	<200	<30
Vanadium	<20	<20	<20	15	<20	15	<20	23
Zinc	58	41	37	60	<10	36	31	48
No. of organic compounds isolated	44	68	67	5	44	1	39	14
No. of reliably identified compounds (% of total)	11(25%)	10(15%)	10(15%)	1(20%)	4(9%)	none	7(18)	3(21%)
Phosphoric acid esters	3	2	3	nd	2	nd	2	nd
Galaxolide	1	1	1	nd	Nd	nd	nd	nd
Chloroform	(1)	na	(1)	nd	(1)	nd	(1)	nd
Ethene, tetrachloro-	nd	nd	(1)	nd	Nd	nd	nd	nd
Phenobarbital	1	nd	1	nd	Nd	nd	nd	nd
Benzamide, N,N-diethyl-3-methyl- (DEET)	1	1	1	nd	Nd	nd	nd	nd
4-Piperidinone, 2,2,6,6-tetramethyl-	1	1	nd	nd	Nd	nd	nd	nd
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	1	1	1	nd	Nd	nd	nd	nd
2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (Irganox 1076)	1	nd	1	1	Nd	nd	1	nd
1H-1,2,4-Triazole-3-carboxaldehyde, 5-methyl-	1	nd	nd	nd	Nd	nd	nd	nd
5,6-Dihydro-6-hydroxy-5-(2,2,6,6- tetramethyl-4-oxo-1-piperidinyl)-thymine--N'-oxide	nd	1	nd	nd	Nd	nd	nd	nd
Carbamazepine	nd	1	nd	nd	Nd	nd	nd	nd
3,4,5,6-Tetramethyl-2-pyridone	nd	1	nd	nd	Nd	nd	nd	nd
1-Piperidinyloxy, 2,2,6,6-tetramethyl-4-oxo-	nd	1	nd	nd	Nd	nd	nd	nd
2H-1-benzopyran-2-one, 7-(diethylamino)-4-methyl-	nd	nd	nd	nd	Nd	nd	1	nd
Benzoic acid, 4-ethoxy-, ethyl ester	nd	nd	nd	nd	Nd	nd	1	nd
Aliphatic hydrocarbons	nd	nd	nd	nd	1	nd	1	nd
Benzene, 1-methyl-2-[(4-methylphenyl)methyl]-	nd	nd	nd	nd	Nd	nd	nd	1

PAHs	nd	nd	nd	nd	Nd	nd	nd	1
Phenol, 4-methyl-	nd	nd	nd	nd	Nd	nd	nd	1

Table 11. Organic compounds identified, and concentrations of metals, in samples of wastewater, river water and river sediments collected in the city of Yaroslavl and the city of Rybinsk, Russia, 2010. Concentrations of metals in water samples are reported in µg/l as total concentrations in the whole (unfiltered) sample. Concentrations of metals in sediments are reported as mg/kg dry weight; nd – not detected; na – not analysed; (#) - signifies number of compounds identified at trace levels using a selective SIM method.

Wastewater from another unidentified discharge RU10025 collected downstream of Polyot Cultural Centre was not significantly contaminated with any of the metals quantified in this study. The sediment sample RU10026 collected about 50m downstream of this discharge contained, however, nickel at 134 mg/kg that is higher than levels typically found in uncontaminated freshwater sediments, which are commonly below 60 mg/kg (ATSDR 2005a). The origin of elevated levels of nickel in the river sample is unknown, but sediments may accumulate pollutants discharged over a long period of time and reflect, therefore, a historic contamination.

Seven organic compounds have been reliably identified among 39 which were isolated from the wastewater sample RU10025 including:

- two esters of phosphoric acid, triphenyl and tributyl phosphates;
- chloroform at 8µg/l
- 2,6-Di-(1,1-dimethylethyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, the phenolic antioxidant (trade name Irganox 1076), which also could be formed as a result of catalytic transformation of another antioxidant butylhydroxytoluene (BHT);
- 7-(diethylamino)-4-methyl-2H-1-benzopyran-2-one, an industrial chemical also known as Fluorescent Brightener 52
- an ethyl ester of 4-ethoxy benzoic acid, which is used as an important component in the catalytic systems for the production of polypropylene.

It is impossible to speculate about the origin of contaminants in these two unidentified discharges, nevertheless, it is likely that they carry, at least a portion of, the wastes from industrial sector of the Rybinsk city. Therefore, it is important to further investigate the sources of organic contaminates released into the River Volga through these two discharges.

Moscow and River Moskva

Kuriyanovskie WWTP and Moscow

Six samples were taken in the vicinity of the Kuriyanovskie WWTP of Moscow city which discharges treated wastewater into River Moskva: two control river sediment samples collected about 500m upstream of the plant: RU10028 (from the left bank) and RU10030 (from the left bank); a single sample of wastewater RU10027 collected at the location of an underwater discharge; river sediment RU10029 collected from the right river bank (opposite side of the plant); and two samples collected downstream of the plant – river water RU10031 and sediment RU10032 (from the left river bank). A single sediment sample RU10033 was collected from the River Moskva just downstream of the official boundary of Moscow city. Results for these samples are summarized in Table 12.

River Moskva upstream of Kuriyanovskie WWTP

One sediment from the river upstream of the WWTP (RU 10028) contained concentrations of copper at 134 mg/kg, of zinc at 185 mg/kg and lead at 40 mg/kg, which is about 3 times higher for copper and slightly above for zinc and lead than levels typically found in uncontaminated freshwater sediments (ATSDR 2004, 2005b & 2007respectively. The second upstream sediment RU 10030 also contained concentrations of copper at 67 mg/kg and zinc at 281 mg/kg, again, higher than levels typically found in uncontaminated freshwater sediments. Levels in uncontaminated freshwater sediments are commonly below 50 mg/kg for copper, 100 mg/kg for zinc and 30 mg/kg for lead (ATSDR 2004, 2005b & 2007).

High loads of organic compounds were detected in sample RU10028 (137 organic compounds were isolated) and, to a lesser extent, in sample RU10030 (30 organic compounds were isolated). Among compounds reliably identified in sample RU10028 were the following:

- fifteen representatives of PAHs;
- five steroid compounds;
- *p,p*-DDT and its metabolite *p,p*-DDD.

Sediment RU10030 did not contain DDT and its metabolite, however, two steroid compounds and one o PAH derivative were also detected in this sample together with several aliphatic hydrocarbons. The range of compounds detected in these river sediments may indicate historical input as a result of both industrial and/or agricultural activity in the upper part of the river, which needs to be further investigated.

Kuriyanovskie WWTP underwater discharge point

Wastewater sample RU10027 was not significantly contaminated with any of the quantified metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. Though, it is important to note that some dilution by surface water during sampling cannot be ruled out. However, despite the fact that this sample was partially diluted with the river water, it still contained reasonably high load of organic compounds from which only a fraction could be reliably identified. The latter included the same compounds which were detected in other wastewater samples investigated in this study (RU10019-21 from Yaroslavl WWTP) including Galaxolide, Surfynol 104, insect repellent DEET, and chlorinated phosphorous flame retardant tri(2-chloroethyl) phosphate. Additionally, this sample contained two non-chlorinated esters of phosphoric acid, tributyl and triphenyl phosphates; pharmaceutical carbamazepine, and traces of VOC tetrachloroethene (at 1µg/l). The presence of these compounds is clearly indicative of insufficient treatment of wastewater by this facility which would have to be significantly upgraded in order to protect natural water resources from ongoing contamination.

The concentrations of the quantified metals in the river sediment RU 10029 collected near the WWTP underwater discharge were within the typical ranges reported for these metals in uncontaminated river sediments. Organic compounds detected in this sample were only two aliphatic hydrocarbons and 28-Nor-17.alpha.(h)-hopane, a representative of pentacyclic triterpanes, which may originate from crude oil or petroleum and which has been reported in sewage sludges (Stronguiló *et al.* 1994).

River Moskva downstream of Kuriyanovskie WWTP

Both river water sample RU 10031 and sediment RU 10032 contained quantified metals at levels typical for these metals in uncontaminated river water and sediments or were below limits of detection for the methods used.

In contrast, river water sample RU10031 showed the presence of organic contaminants detected in the wastewater sample from Kuriyanovskie WWTP (RU10027), namely:

- Galaxolide;
- insect repellent DEET;
- and three esters of phosphoric acid including tributyl, thriphenyl and tri(2-chloroethyl) phosphates.

This finding indicates that Kuriyanovskie WWTP is most likely the main contributor of detected organic contaminants to water pollution of the River Moscow at the investigated site. This needs, however, to be further confirmed by more detailed investigation including analysis of water samples collected in the upper part of the river before it reaches Kuriyanovskie WWTP. It is also important to note, that similar ranges of organic contaminants have been detected in other wastewater samples investigated in the current study - from Yaroslavl WWTP (RU10019-RU10021), which shows that such pollutants are not retained or degraded by existing treatment techniques and may enter receiving watercourses. River water sample RU10031 also contained the plasticizer diisobutyl phthalate, two isomers of chlorinated flame retardant Fyrol PCF, and phenanthrene. Sediment sample RU10032 contained only limited number of aliphatic hydrocarbons.

River Moskva downstream of the Moscow city

River sediment RU 10033 collected from Moskva River downstream of the official boundary of Moscow City contained zinc at a concentration of 147 mg/kg, slightly higher than typical background levels of about 100mg/kg. The only organic compounds detected in this sample were representatives of aliphatic hydrocarbons.

Sample	**RU10027**	**RU10028**	**RU10029**	**RU10030**	**RU10031**	**RU10032**	**RU10033**
Type	**waste water**	**sediment**	**sediment**	**sediment**	**River water**	**sediment**	**sediment**
Location	Kuriyanovskie WWTP	River Moskva, upstream RU10027, left bank	River Moskva, next to RU10027	River Moskva, upstream RU10027, right bank	River Moskva, 500 m downstream Kuriyanovskie WWTP from fairway	River Moskva, 500 m downstream Kuriyanovskie WWTP, left bank	River Moskva, left shore. After Moscow circle road bridge.
METAL	µg/l	mg/kg	mg/kg	mg/kg	µg/l	mg/kg	mg/kg
Antimony	<50	<20	<20	<20	<50	<20	<20
Arsenic	<50	<20	<20	<20	<50	<20	<20
Barium	21	78	47	144	26	95	103
Cadmium	<5	1	<1	1	<5	<1	<1
Chromium	<20	68	23	51	<20	24	42
Chromium (VI)	-	-	-	-	-	-	-
Cobalt	<20	4	4	8	<20	7	8
Copper	<20	134	32	67	<20	13	38

Lead	<50	40	11	22	<50	6	16
Manganese	42	132	218	210	43	505	318
Mercury	<2	<0.5	<0.5	<0.5	<2	<0.5	<0.5
Nickel	<20	15	9	23	<20	14	21
Selenium	<200	<30	<30	<30	<200	<30	<30
Vanadium	<20	16	14	25	<20	23	25
Zinc	39	185	96	281	48	78	147
No. of organic compounds isolated	57	137	25	30	42	29	20
No. of reliably identified compounds (% of total)	9(16%)	17(12%)	3(12%)	11(37%)	8(19%)	6(21%)	12(60)
Phosphoric acid esters	3	nd	nd	nd	5	nd	nd
Galaxolide	1	nd	nd	nd	1	nd	nd
Benzamide, N,N-diethyl-3-methyl- (DEET)	1	nd	nd	nd	1	nd	nd
DiBP		nd	nd	nd	1	nd	nd
Carbamazepine	1	nd	nd	nd	nd	nd	nd
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	1	nd	nd	nd	nd	nd	nd
2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (Irganox 1076)	1	nd	nd	nd	nd	nd	nd
Ethene, tetrachloro-	(1)	nd	nd	nd	nd	nd	nd
PAHs and derivatives	nd	nd	nd	nd	1	nd	nd
Steroids	nd	5	nd	2	nd	nd	nd
DDT & metabolites	nd	2	nd		nd	nd	nd
Aliphatic hydrocarbons	nd	nd	2	8	nd	6	12
PAH & derivatives	nd	12	nd	1	nd	nd	nd
28-Nor-17.alpha.(h)-hopane	nd	nd	1	nd	nd	nd	nd

Table 12. Organic compounds identified, and concentrations of metals, in samples of wastewater and sediments associated with Kuriyanovskie WWTP, Moscow, Russia, 2010. Concentrations of metals in water samples are reported in µg/l as total concentrations in the whole (unfiltered) sample. Concentrations of metals in sediments are reported as mg/kg dry weight; nd – not detected; (#) - signifies number of compounds identified at trace levels using a selective SIM method.

Conclusions

The current study investigated selected aspects of pollution in rivers of the Russian Federation including those which receive substantial amount of wastewaters direct from industry and *via* common wastewater treatment plants (WWTP). In April-May 2010, Greenpeace collected thirty one samples including river water, sediments and wastewaters from industrial and WWTP discharges into the following rivers: Syas, Svir`, Sheksna, Koshta, Volga, and Moskva. Sample of surface water from the Krasny Bor toxic waste landfill drainage canal was also collected. From the current study, it is evident that highly complex wastes containing a variety of toxic chemicals are being discharged of into natural watercourses.

Leningradskaya Oblast

Analysis of effluent from the Syasskiy pulp and paper mill in Leningradskaya Oblast, which

is discharged into Ladoga Lake, showed the presence of numerous pollutants including chlorinated organic compounds which are formed during pulp bleaching (e.g. chlorinated phenols, chlorinated guaiacols, chloroform). Such effluents have the potential to seriously impact environmental quality and hence the health of both humans and wider ecosystems. To prevent further deterioration of the surrounding environment, it is necessary to convert to a totally chlorine-free (TCF) pulp bleaching process which eliminates the generation of chlorinated compounds in associated wastes.

Surface water from the canal around the Krasny Bor polygon, the toxic wastes landfill, contained a wide range of toxic organic chemicals including pesticides, herbicides, pharmaceuticals, chlorinated phenols, chlorinated benzenes, chlorinated alkanes, and chlorinated phosphorus-organic flame retardants. This finding is very alarming taking into account the fact that these pollutants were present in soluble form, and could be potentially transported by receiving watercourses (River Maly Izhorets), but also migrate through soils and sediments to the wider environment. Re-volatilisation and atmospheric distribution of pollutants detected at this site cannot be also ruled out.

Vologodskaya Oblast

In Vologodskaya Oblast, high concentrations of zinc and, to a lesser extent, cadmium, copper and lead were found in sediments of the River Koshta downstream of the Severstal Industrial Estate located in Cherepovets city, one of the most significant industrial centers in the north-west of Russia. A range of polycyclic aromatic hydrocarbons (PAHs), which are toxic to humans, animals and aquatic life were also detected there.

A high concentration of arsenic was detected in the wastewater originating from the JSC Ammofos artificial waste lagoon discharging into the River Koshta exceeding levels for this element commonly found in uncontaminated waters by up to nine times. The source of arsenic in these waters is unclear and needs to be further investigated.

Yaroslavlskay Oblast

A range of pollutants, some of which are persistent and/or toxic compounds, were detected in the wastewater samples from the main Yaroslavl WWTP. This discharges directly into the Volga River. Chemicals found included chlorinated phosphorus flame retardants, nonionic surfactants, a polycyclic synthetic musk, pharmaceutical chemicals, and disinfection by-products. This analysis revealed that treatment of wastewater on the Yaroslavl WWTP does not prevent these pollutants from being discharged to the River Volga; this facility is acting as a significant point source of organic pollutants to the environment downstream.

The analyses of water discharged to the River Volga from two unidentified discharges located within the city of Rybinsk revealed the presence of contaminants which are likely to have originated from the industrial sector including chlorinated esters of phosphoric acid, antioxidants, and chloroform. Elevated levels of nickel were also detected in water from one of discharges and in associated sediment from the River Volga. It is important to further investigate the sources of contaminants released into the River Volga through these two discharges.

Moscow

The effluents from Kuriyanovskie WWTP discharging to the River Moskva through the submerged outlet contained a range of pollutants similar to those detected in wastewater

samples from Yaroslavl WWTP, which shows that such pollutants are not retained or degraded by existing treatment techniques. The WWTP would have to be significantly upgraded in order to protect natural water resources from ongoing contamination.

Additionally, the contamination of sediment samples collected from the River Moskva upstream of Kuriyanovskie WWTP was also of concern. Elevated levels of several heavy metals were detected there including copper, zinc and lead. Numerous representative of polycyclic aromatic hydrocarbons (PAHs) and steroid compounds were detected at one of the two investigated sites together with *p,p*-DDT and its metabolite *p,p*-DDD. The range of compounds detected in these river sediments may indicate historical input as a result of both industrial and/or agricultural activity in the upper part of the river, which needs to be further investigated.

References

ACAP (2005) Assessment of Mercury Releases from the Russian Federation. Reduction of Atmospheric Mercury Releases from Arctic States. Danish EPA, Copenhagen, 2005

Ali, M., Sreekrishnan, T. R. (2001) Aquatic toxicity from pulp and paper mill effluents: a review. Advances in Environmental Research 5(2): 175-196

Ali, M., Sreekrishnan, T. R. (2001) Aquatic toxicity from pulp and paper mill effluents: a review. Advances in Environmental Research 5(2): 175-196

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 nickel. Agency for Toxic Substances and Disease Registry, US Public Health Service, August 2005

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

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

ATSDR (2007b) Toxicological profile for arsenic. United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007 http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=22&tid=3

BFN (2008) Land-locked Salmon in the Ladoga and Onego basins Dr. Sergey Titov, Dr. Dmitry Sendek, Dr. Igor Schurov, Baltic Fund for Nature, Saint Petersburg 2008

FAF RF (2010) On the adoption of quality norms of fisheries water objects, including norms of maximum permissible levels of hazardous substances in water of fisheries water objects. Federal Agency for fisheries for the Russian Federation. Order № 20, 18th of January 2010

Government RF (1999) Decree "On the adoption of the rules of water supply and sewerage in the Russian Federation", adopted by the Government of the Russian Federation by the decree # 167 from the 12th of February 1999 amended in 2006

HELCOM (2010) HELCOM 2010, BALTHAZAR project 2009-2010: Reducing risks of hazardous wastes in Russia

Johnston, P.A., Stringer, R.L., Santillo, D., Stephenson, A.D., Labounskaia, I. Ph., McCartney, H.M.A. (1997) Towards zero-effluent pulp and paper production: The pivotal role of totally chlorine free bleaching. Greenpeace Report Executive Summary. Environmental Science and Pollution Research 4 (3): 130

JSC Yaroslavlvodokanal (2011) JSC Yaroslavlvodokanal official web-page, www.yvk.ru, accessed on the 11th of May, 2011

Krasny Bor (2011) Official web-page of the Krasny Bor poligon, http://redbor.narod.ru/index.htm, observed on the 10th of May 2011

Kukkonen, J.V.K., Eadie, B.J., Oikari, A., Holmbom, B. & Lansing, M.B. (1996) Chlorophenolic and isotopic tracers of pulp mill effluent in sedimenting particles collected from southern lake saimaa, Finland. Science of the Total Environment 188(1): 15-27

Labunska, I., Brigden, K., Santillo, D., Kiselev, A. & Johnston, P. (2010). Russian Refuse2: an update on PBDEs and other contaminants detected in St-Petersburg area, Russia. Greenpeace Research Laboratories Technical Note 04/2010

Lacorte, S., Latorre, A., Barceló, D., Rigol, A., Malmqvist, A., Welander, A. T. (2003) Organic compounds in paper-mill process waters and effluents. TrAC Trends in Analytical Chemistry 22(10): 725-737

Li, W., Peng, Y., Shi, J., Qiu, W., Wang, J., Bai Z. (2011) Particulate polycyclic aromatic hydrocarbons in the

urban Northeast Region of China: Profiles, distributions and sources. Atmospheric Environment, In Press, Corrected Proof, Available online *Available online 13 April 2011*
Martel, P.H., Kovacs, T.G., O'Connor, B.I., Voss R.H. (1994) A survey of pulp and paper mill effluents for their potential to induce mixed function oxidase enzyme activity in fish. Water Research 28(8): 1835-1844
MPR&E RF (2010). "The state of environment in Russian Federation in 2009", Ministry for the natural resources and the environment for the Russian Federation, Moscow, 2010
MSUE Mosvodokanal (2011) Moscow state unitary enterprise Mosvodokanal official web-page www.mosvodokanal.ru, observed on the 11th of May, 2011
NLBVU (2010) Nevsko-Ladozhskoe BVU, Data about allotments of water objects in accordance with agreements with water users and conclusions on allotments of the water objects in the area of operations of Nevsko-Ladozhskoe BVU on 30.12.2010
Olaniran, A. O., Igbinosa. E. O. (2011) Chlorophenols and other related derivatives of environmental concern: Properties, distribution and microbial degradation processes. Chemosphere 83(10): 1297-1306
Orrego, R., Pandelides, Z., Guchardi, J., Holdway D. (2011) Effects of pulp and paper mill effluent extracts on liver anaerobic and aerobic metabolic enzymes in rainbow trout. Ecotoxicology and Environmental Safety 74(4):761-768
Ritchlin, J. & Johnston, P. (1998). Zero Discharge: Technological progress towards eliminating Kraft pulp mill liquid effluent, minimising remaining waste streams and advancing worker safety. Publ: Reach for Unbleached Foundation, Canada. ISBN 0-9680431-2-7: 51 pp.
RTP (1994) The Science of Chlorine. Chapter 6: Pulp and paper Regulatory Toxicology and Pharmacology 20(1) Part 2: S308-S415
Severstal (2011) Severstal official web-page, http://www.severstal.com/eng/about/company_history/, observed on the 11th of May, 2011
Stringer, R. & Johnston, P. (2001) Chlorine and the environment: and overview of the chlorine industry. Chapter 5. Pulp and paper production. Kluwer Academic Publishers, The Netherlands. pp107-132
Stronguiló, M.L., Vaquero, M.T., Comellas, L.& Broto-Puig, F. (1994) The fate of petroleum aliphatic hydrocarbons in sewage sludge-amended soils. Chemosphere 29(2): 273-281
The Sun (2010). The Sun, Published on the 06th of November 2010, accessed on the 11th of May, 2011
Thompson, G., Swain, J., Kay, M., Forster, C. F. (2001) The treatment of pulp and paper mill effluent: a review. Bioresource Technology 77(3): 275-286
USPHS (1997). Toxicological profile on CD-ROM. Agency for Toxic Substances and Disease Registry
Zhang, Y., Ma, C., Ye, F., Kong, Y., Li H. (2009) The treatment of wastewater of paper mill with integrated membrane process. Desalination 236(1-3): 349-356

Appendix. Analytical methodology

Analysis for Volatile Organic Compounds (VOCs)

Method

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 35^0C (held for 4min), rising to 55^0C at 5^0C/min, and then to 210^0C at 15^0C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method.

Halogenated VOCs quantified in the water samples with limits of detection and quantification are presented in Table 5.

Quality control
Limits of quantification (LOQ) were determined as the lowest concentration in the linear regression used for quantification. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. 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.

Compound	LOQ, µg/l	r^2
Vinyl chloride	1	0.999
Methane, dichloro-	1	0.992
Ethene, 1,2-dichloro-, trans-	2	0.999
Ethene, 1,2-dichloro-, cis-	1	0.999
Chloroform	1	0.998
Ethane, 1,1,1-trichloro-	1	1.000
Benzene	1	0.999
Ethane, 1,2-dichloro-	1	0.998
Ethene, trichloro-	1	0.998
Toluene	1	1.000
Ethene, tetrachloro-	1	0.996
Benzene, chloro-	2	0.996
m- & p-Xylene	2	0.999
o-Xylene	2	1.000
Toluene, 2-chloro-	2	0.999

Table. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r^2 – corresponding correlation coefficient) used for quantification.

Analysis for extractable organic compounds

Preparation
20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. For sediment samples, approximately 10 g of each sample (wet weight) was extracted employing Accelerated Solvent Extraction (ASE) technique using Dionex ASE-350 with a mixture of pentane and acetone 3:1, at a temperature of 100°C. Water samples (500ml) were prepared using solid phase extraction technique with Dionex AutoTrace workstation, eluting solvents were ethyl acetate followed by a mixture of pentane and toluene 95:5. Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.
Clean-up procedures were the same for the crude extracts from both aqueous and sediment samples. Each extract was shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 1ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis
For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with 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. The GC oven temperature program employed was as follows: an initial temperature of 35^0C, held for 2 minutes, raised to 260^0C at 10^0C/min, then to 320^0C at 6^0C/min (held for 8min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times 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.

Quality control
A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory.

Analysis for metals

Preparation
A representative portion of each sediment sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5g of each sample was digested with 2 ml concentrated hydrochloric acid and 8 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180ºC over 15 minutes followed by holding at 180ºC for a further 15 minutes. Following cooling, digests were filtered and made up to 50ml with deionised water.

For water samples, to obtain total concentrations, a representative portion of each whole sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. In addition, a portion of each whole sample was filtered and then acidified in the same way. 50 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180ºC over 15 minutes followed by holding at 180ºC for a further 15 minutes. Cooled digests were filtered and made up to 50 ml with deionised water.

Analysis
Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 10 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury content in the samples was carried out separately. Mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample 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.

Quality control
For sediment samples, two samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China, and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

For water samples, three samples were prepared in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water), and a mixed metal quality control solution of 4 mg/ l, other than mercury at 80 µg/l. All 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 at 8 mg/l and 0.8 mg/l (sediment samples) or 4 mg/l and 0.4 mg/l (water samples) prepared in an identical manner but from different reagent stocks to the instrument calibration standards. For cold vapour generation mercury analysis, the calibration was validated using two quality control standards (10 µg/l and 80 µg/l), prepared internally from different reagent stock.

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