Bull Environ Contam Toxicol (2009) 83:776–779
DOI 10.1007/s00128-009-9798-1

Assessment of the Amur River Ecosystem Pollution with Benzene and Its Derivatives Caused by an Accident at the Chemical Plant in Jilin City, China

S. I. Levshina · N. N. Efimov · V. N. Bazarkin

Received: 29 July 2008 / Accepted: 14 June 2009 / Published online: 2 July 2009

Abstract Assessment of concentrations of benzene and its derivatives in the Amur water and fish caught in summer and autumn 2006 was carried out after Jilin chemical plant accident (winter 2005) in the People's Republic of China. Fish sampling of *Leiocassis ussuriensis* conducted in the Amur River near Khabarovsk identified benzene, toluene, ethylbenzene, isopropylbenzene, xylene reaching to 16, 98.7, 55, 54, and 206 μg kg^{-1}, respectively. For *Hypophthalmichtys molitrix Valenciennes* sampled in the lower reaches of the Amur benzene, toluene, ethylbenzene, xylene were found in amounts to 9, 15.4, 16 μg kg^{-1}, and, benzene and xylene reaching 6 and 16 μg kg^{-1} were found in *Huso dauricus* and benzene and xylene of 2–6 and 13–16 μg kg^{-1}, respectively, in *Acipenser schrenckii*. The above toxicants were not detected in the Amur water near the river mouth in autumn 2006.

Keywords The Amur River · The Songhua River · Fish · Pollution

Over recent decades the Amur River has been subjected to heavy transboundary pollution. The Songhua River, its largest right-bank tributary, flows entirely through the Chinese territory. Its share in the Amur River runoff is about 25%. The Jilin chemical plant explosion occurred on November 13, 2005, resulted in massive spill ingress of 100 tons of poisonous chemical substances (benzene, nitrobenzene, sulfuric acid and other compounds) and created an 80 km long toxic slick in the Songhua River, a tributary of the Amur. The slick, predominantly made up of benzene and nitrobenzene, passed through the Amur River over subsequent weeks. In December 2005 the Songhua River toxic chemicals spill reached the Amur River. Monitoring of the spill became particularly difficult with river freeze-up. To prevent the contamination of the water inlets in Khabarovsk, a special dam was constructed in the Amurskaya sub-channel which was dismounted in spring 2006.

In contrast to its homologues (toluene and xylenes) benzene is extremely resistant to biological oxidation and tends to accumulate in living organisms, thus being a very toxic cumulative poison (Henderson et al. 1989; Medinsky et al. 1989). It is lighter than water (its density measured at 20°C is 0.879) and is practically insolvable (0.08%).

The present study aims at the detection and assessment of concentrations and dynamics of benzene and its derivatives in water and hydrobionts of the Amur after the ecological catastrophe in the Songhua basin.

Materials and Methods

The research is based on the data obtained in spring and autumn 2006, a year and a half after the accident. To collect water samples in the Amur River and the Amurskaya sub-channel a 1-L bathometer was used. Samples were collected from the surface (0.5 m) and bottom (0.5 m) water horizons in all the three hydrologic sections (the left and right banks and the middle of the river) except for Station 7, where only surface water samples were taken

S. I. Levshina (✉) · V. N. Bazarkin
Institute of Water and Ecology Problems,
Far Eastern Branch, Russian Academy of Sciences,
65 Kim Yu Chen St., 680000 Khabarovsk, Russia
e-mail: levshina@ivep.as.khb.ru

N. N. Efimov
Amur Branch of WWF-Russia,
18-a Verchneportovaya, 690091 Vladivostok, Russia

(Fig. 1). The collected samples were stored in dark-glass bottles at +4°C. Totally 70 water samples have been analyzed.

Fish sampling was conducted in the Amur River near Khabarovsk (St. 4) (*Leiocassis ussuriensis*, *Hypophthalmichtys molitrix Valenciennes*, *Hemibarbus maculatus Bleeker*); in feeding and spawning areas 5–7 km upstream Nickolaevsk-na-Amure (St. 7) (Sturgeon species *Acipenser schrenckii* and Kaluga species *Huso dauricus*) and in hunchback salmon spawning areas (St. 7) (*Oncorhynchus gorbuscha*). Muscle tissue was sampled from each of the fish. Liver and gonads (soft roe or hard roe) were additionally sampled from Sturgeon species. Samples were stored in the freezer (−10°C). Forty-four fish samples were caught, 20 of them were sturgeon and 10 were salmon species. Totally 94 tissue samples have been examined.

Along with sturgeon fish sampling, a number of mollusk samples (bivalves and gastropods) were simultaneously collected. These mollusks are the feeding base for Sturgeon species. Soft mollusk tissue bodies have been analyzed (Sokolov and Levshina 2007).

Water and ice samples were analyzed for benzene, toluene, μ-, n-xylenes, o-xylene, ethylbenzene, isopropylbenzene (cumene) applying a gas chromatography method under the International Standard ISO 11423-1. The Shimadzu GC-2010 chromatographer was used (Fomin 2000). Calibration solutions were prepared from standard samples. Systematic bare tasting was used to control the analysis. Method sensitivity was 0.1 μg L^{-1}. Fish and mollusk tissue were analyzed under Standards MI 4.1.765-99 (Methodic Instructions 1999). The analysis sensitivity was 0.1 μg L^{-1}.

According to the Index of Fishing Industry Norms (Index 1999) the permissible concentration level (PCL) of benzene, toluene, isopropylbenzene, xylenes and ethylbenzene in fisheries waters should not exceed 0.5, 0.5, 0.1, 0.05 and 0.001 mg L^{-1}, respectively.

Results and Discussion

During the toxic chemicals spill passing along the Amur River in November–December 2005 benzene trace concentrations were registered. As the river freeze-up occurred benzene froze at the ice bottom. Thus, concentrations of benzene, toluene, ethylbenzene and xylenes, were 0.11–1.09, 1.56–1.97, 1.40 and 1.00 μg L^{-1}, respectively, in ice samples collected from the Amur cross section upstream Khabarovsk (St. 3). Maximal concentrations of these substances were registered at the bottom edge of 10-cm thick ice core samples taken in the middle of the river and at the right (Chinese) bank.

In spring 2006 benzene and its derivatives were not identified in the Amur River upstream of the Songhua River mouth (St. 1). Benzene was registered in the Amur

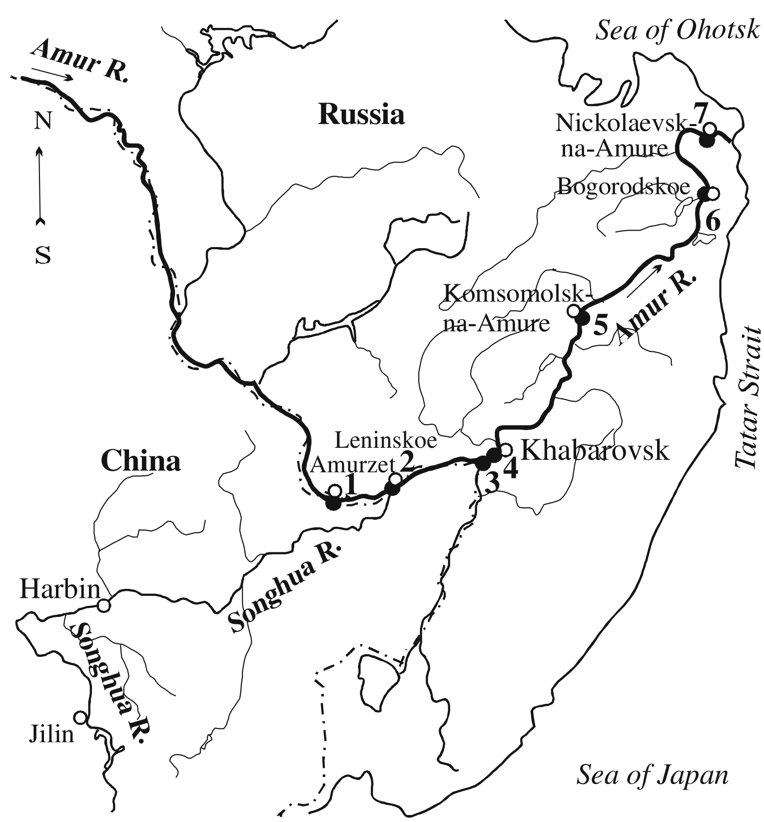

Fig. 1 Stations of water, ice and bottom sediment sampling

water at the confluence of the Songhua River mostly in the middle of the river and at the right (Chinese) bank. Its concentrations decreased gradually downstream from Station 2 (3.13 μg L^{-1}) to Station 4 (0.53 μg L^{-1}), and farther to Station 5 (0.45 μg L^{-1}) (Levshina 2007). Xylenes were found in water of the Amurskaya sub-channel (Fig. 2). Their maximal concentrations of 22 μg L^{-1} or ~0.5 PCL were observed in the ice-break period (April 20, 2006) as caused by contaminated ice-melt waters. In the following 10 days xylene concentrations decreased by an order of magnitude and subsequently dropped to zero. Later on xylene was observed in water only in single cases after rainfalls (the end of May, 2006). It resulted from washing out of contaminated ice from the Amur River banks.

In autumn 2006 (September–October) although benzene was not registered in the Amur water, some of its derivatives were identified at concentrations lower than the PCL. For example, in Bogorodskoe (St. 6), small concentrations of isopropylbenzene and xylenes were detected. As for Station 7, no toxicants were found here in autumn 2006. It was established that benzene does not concentrate in water biota (Trucco et al. 1983) and quickly disappears from fish,

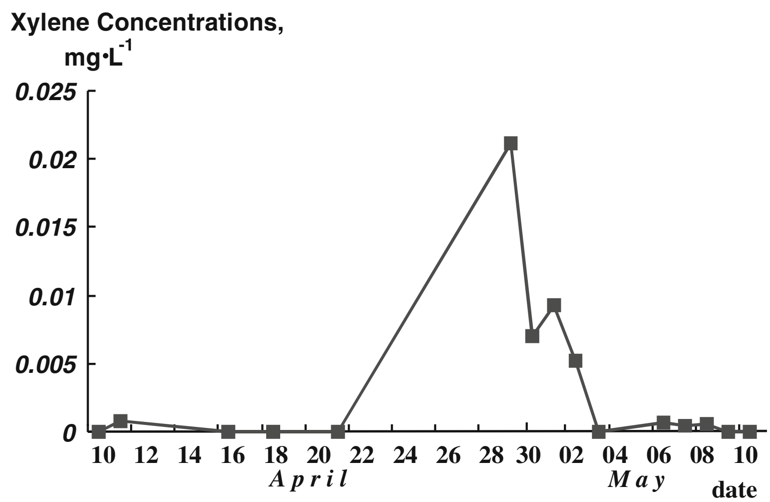

Fig. 2 Xylene concentrations in water of the Amurskaya sub-channel (St. 3) in spring 2006

Table 1 Content of benzene and its derivatives in tissue and organs of fish caught in the Amur in summer and autumn 2006, μg kg^{-1} (wet weight)

Station no.	Number of samples	Tissue type	Compound				
			Benzene	Toluene	Ethylbenzene	Isopropylbenzene	*o*, *μ*, *n*-Xylene (total)
Leiocassis ussuriensis							
4	6	F	10–16/5	9–987/3	49–55/3	25–54/3	67–206/5
Hypophthalmichtys molitrix Valenciennes							
4	4	F	5–7/3	1.5–22.1/3	–	–	52–149/3
	4	L	8–9/3	2–25/3	–	–	–
Hemibarbus maculatus Bleeker							
4	5	F	–	–	–	–	–
	5	L	–	–	–	–	–
Huso dauricus							
7	10	F	–	–	–	–	12/1
	10	L	–	–	–	–	15/1
	10	G	–	–	15.4/1	–	15–16/2
Acipenser schrenckii							
7	10	F	6/1	–	–	–	16/1
	10	L	2/1	–	–	–	15/1
	10	G	3/1	–	–	–	13/1

F, fish fillet; L, liver; G, gonads; –, not discovered; under (/), toxicant occurrence

Norm documents that regulate concentrations of these components in fish are not enacted in Russia when it is put in clean water (Ogata and Miyake 1978). In our studies of fish, caught in summer 2006 in the Amur near Khabarovsk (St. 4), we detected significant concentrations of benzene and its derivatives in fish tissue and liver; maximal toxicant concentration was found in *Leiocassis ussuriensis*. Benzene and xylene total concentrations reached 18.4 and 200 μg kg^{-1}, respectively (Table 1). Benzene, toluene and xylenes were also found in *Hypophthalmichtys molitrix Valenciennes* and their concentration in fish liver was higher than in muscle tissue. In *Hemibarbus maculatus Bleeker* and *Oncorhynchus gorbuscha* no toxicants were revealed.

Studies of sturgeon species of the lower Amur River (St. 7) revealed the presence of benzene in one sturgeon sample (*A. shrenkii*) only, but it was registered in all its organs. Maximal benzene concentrations (6 μg kg^{-1}) were observed in fish fillet whereas in liver and hard roe they were 2 and 2.5 times lower, respectively. In two other sturgeon samples *o*-xylene was found (13–16 μg kg^{-1}) in tissue, liver and soft roe. Kaluga (*Huso dauricus*) studies detected the presence of *o*-xylene (12–16 μg kg^{-1}) and ethylbenzene (15 μg kg^{-1}) in soft roe of two samples. In general, toxicants (benzene, ethylbenzene and xylenes) were registered in 5 fish samples practically in all the studied organs. Isopropylbenzene concentrations of 10.3–12.5 μg kg^{-1} were found in 5 out of 16 samples of bivalves (Sokolov and Levshina 2007).

Conclusion

The ecological catastrophe on the Amur in 2005 produced a negative impact not only on water quality, but also on the state of the entire ecosystem. The following facts make evidences of it: benzene derivatives were identified in the fish, caught in the Amur near Khabarovsk, and also in sturgeon species (*Huso dauricus, Acipenser schrenckii*) and bivalves (*Sinanodonta likharevi, Cristaria herculea*) which were collected 1.400 km lower the Songhua River mouth 9 months after the Jilin accident. Natural waters contained neither benzene nor its derivatives at that time. The assessment of a cumulative impact of pollutants present in river water ecosystem due to multi-year chronic pollution appears to be an urgent task for future studies.

Acknowledgments The authors are grateful to WWF International for the financial support of the salmon and mollusk research project "Understanding Effects of Transboundary Benzene Pollution on the Amur and Kaluga Sturgeon, No D449/9S077600/GLM".

References

Fomin GS (2000) WATER control of chemical, bacteriologic and radiation safety according to international standards. Protector, Moscow (in Russian)

Henderson RF, Sabourin PJ, Bechtold WE, Griffith WC, Medinsky MA, Birnbaum LS, Lucier GW (1989) The effect of dose, dose rate, route of administration, and species on tissue and blood levels of benzene metabolites. Environ Health Perspect 82:9–17

Index of Fishing Industry Norms (1999) Permissible concentration levels (PCL) and approximate safety levels (ASLE) of toxicant effect for water objects of fishing importance. VNIRO, Moscow, p 303 (in Russian)

Levshina SI (2007) Concentration and dynamics of organic matter in Amur and Songhua waters. J Geogr Nat Resour 2:44–51 (in Russian)

Medinsky MA, Sabourin PJ, Henderson RF, Lucier G, Birnbaum LS (1989) Differences in the pathway for metabolism of benzene in rats and mice simulated by a physiological model. Environ Health Perspect 82:43–49

Methodic Instructions (1999) The use of gas chromatography for estimations of aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, *n*- xylene) in biomedia (blood). MI 4.1.765-99. RF Ministry of Health, Moscow, p 24 (in Russian)

Ogata M, Miyake Y (1978) Disappearance of aromatic hydrocarbons and organic sulphur compounds from fish flesh reared in crude oil suspension. Water Res 12:1041–1044

Sokolov AV, Levshina SI (2007) State of fresh water mollusks of the lower Amur under transboundary pollution. Theses, All-Russia Sci Conf NESC, FEB RAS, Magadan, p 187 (in Russian)

Trucco RG, Engelhardt AS, Stacey B (1983) Toxicity, accumulation and clearance of aromatic hydrocarbons in *Daphnia pulex*. Environ Pollut Ser A 31:191–202