MERCURY CONTAMINATION AS A LEGACY OF CHEMICAL PRODUCTION IN THE CEE REGION

Mach, V., Skalský M.[1], Petrlík J.,[1,2], Bell L.[2], Jelínek N.[1]
[1] Arnika – Toxics and waste programme, Prague, Czech Republic
[2] International Pollutants Elimination Network, Sweden

Summary
The Minamata Convention was adopted in 2013 to protect the environment and human health from mercury. Mercury has been known as a pollutant for decades, and the effects on human health associated with its presence in the environment are well known. This toxic metal bioaccumulates particularly in aquatic environments, and through the food chain and, especially through fish and seafood, enters the human body. Even before the Minamata Convention, a threshold by WHO (0.5 mg/kg wet weight) for mercury concentrations in fish was established which should not be exceeded for human consumption. The results of our study show that this concentration is commonly exceeded in fish from the vicinity of former and operating factories using mercury in various processes, chlor-alkali plants in particular. Fish from these areas poses a serious health risk. It also shows that the mercury problem is of global concern due to its transportation from hotspots to distance of tens of kilometres in aquatic environment. Remediation of these sites is also complicated due to the presence of other contaminants such as e.g. POPs.

Key words
chlor-alkali contamination mercury Minamata Convention chemical industry remediation contaminated sites

1 Introduction

Mercury is a substance of global concern due to its long-range transport, persistence, ability to bioaccumulate, and toxicity. The Minamata Convention was adopted in 2013 to reduce mercury transport globally. The chemical industry in the region of Central and Eastern Europe (CEE) left many heavily contaminated sites and polluting factories that are subject to the treaty provisions. This study evaluates mercury contamination in the vicinity of such hot spots.

Impacts of mercury on human health and the environment

Mercury has been well known as an environmental pollutant for several decades. The way mercury affects organism depends on its chemical form and route of exposure. The pathways and fate of mercury in aquatic environments are important because it is in waters, sediments, and wetland soils that inorganic mercury is converted to methylmercury, which concentrates in animals at the top of a food chain, including humans. Once mercury enters a human organism, it acts as a neurotoxin, or negatively impacts the immune system. The majority of human exposure to mercury is from the consumption of fish and marine foods. Thus, the most studies of mercury contamination focus on aquatic ecosystems and mercury levels in fish.

Mercury in chemical industry

There are several manufacturing processes intentionally involving mercury that are recognized by the Minamata Convention on Mercury. These processes are mercury-based chlor-alkali production; sodium and potassium methylate or ethylate production using mercury cell electrolysis; vinyl chloride monomer, acetaldehyde, and polyurethane production using mercury as a catalyst. These applications of mercury in the chemical industry are addressed by Article 5: Manufacturing processes in which mercury or mercury compound are used. Some uses of mercury in chemical industry are to be phased-out while others are to be restricted.

2 Materials and methods

In this study, we present eight case studies focused on contamination with mercury at sites contaminated due to former or recent chemical factories using mercury in the CEE and CIS countries. Geographical locations of the sites are shown in Fig. 1. Some of these sites were remediated already however most of them remain to some extend contaminated. There description is based on previous larger report (Mach et al. 2016). Particular attention is paid to fish contamination at these sites. Levels of mercury in fish were measured in previous studies.

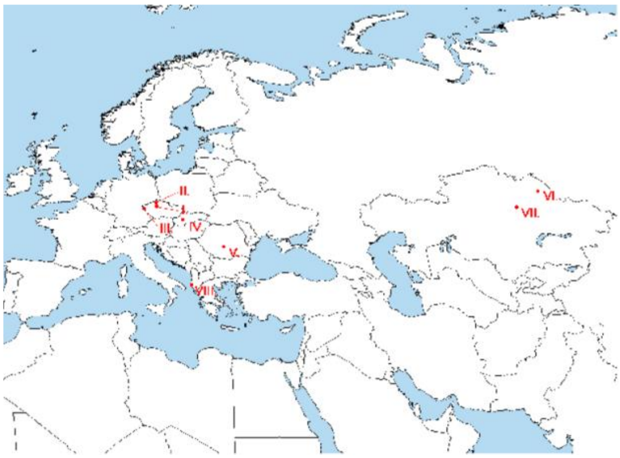

Figure 1: *Localization of the case studies in the CEE and CIS region. I. - Spolana Neratovice, II. - Spolchemie in Ústí nad Labem, III. – Former Marktredwitz Chemical Factory, IV. – Fortischem in Nováky, V. - Oltchim in Râmnicu Vâlcea, VI. - Former Chemical Complex in Pavlodar, VII. - Former chemical factory Karbid in Temirtau, VIII. - Former Soda PVC Plant in Vlora.*

3 Case studies

3. 1 Spolana Neratovice, Czech Republic

Spolana Neratovice is the largest chemical factory in the Czech Republic with a chlor-alkali production plant and plant for manufacturing PVC plastic, located close to the Labe River. There were used graphite electrodes in the old amalgam electrolysis plant. Mercury contamination was observed not only in the Labe River but also in nearby quarry lake Mlékojedy. Angling has a long history in the city of Neratovice and a local group of Czech Fishing Union continued to encourage fish population for angling in the Labe River and Mlékojedy quarry lake despite mercury contamination. Contamination of surrounding environment was very well documented by the study focused on mercury oak bark (see Figure 2 and Table 1).

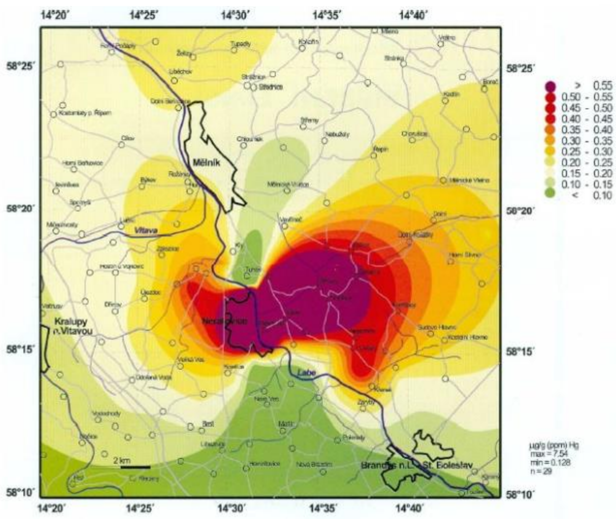

Figure 2: Determined and interpolated mercury concentrations in oak bark in the investigated area in the surrounding of Spolana Neratovice. Source: Suchara et Sucharová 2008.

3. 2 Spolchemie, Czech Republic

Spolchemie is one of the oldest chemical factories in the Czech Republic and one of the two chlor-alkali production plants in the Czech Republic is a part of the Spolchemie chemical complex. Spolchemie is situated on the confluence of the River Labe and River Bílina. Mercury contamination was reported in soils at the area of Spolchemie), in sediments and biofilm of the River Bílina (Pokorný *et al.*, 2011) (see Table 1) and in fish from both the River Labe and the River Bílina (see Figure 3).

3. 3 Marktredwitz, Germany

Marktredwitz Chemical Factory was the oldest chemical production site in and in the world. Marktredwitz is located on the Kössein water stream in the watershed of the Ohře River with Skalka reservoir, which later flows into the Labe River. Despite the expensive decontamination after 200 years of operation of the factory and the discharge of mercury into the Kössein watershed, much pollution remains. Sediments from the Kössein water stream, Reslava and Ohre Rivers pose a secondary source of pollution (see Table 1), especially during floods when the decontaminated sediments enter the Skalka reservoir. Consumption of fish from the Skalka reservoir thus poses a health risk. The fish are contaminated mainly by methyl-mercury (Maršálek *et al.*, 2005).

3.4 Fortischem, Slovakia

Fortischem a.s. is one of the Slovakia's key chemical manufacturing sites in Slovakia and has been identified as one of the "hotspots" near Nitra River. There is a mercury cell chlor-alkali production plant at the site. The first of two studies conducted by Greenpeace Czech Republic (2002) examined two waste-water discharges and related sediment (see Table 1).

3. 5 Oltchim, Romania

Oltchim is one of the largest chemical factories in Romania and the largest chlor-alkali plant in Central and Eastern Europe located close to Babeni Reservoir on River Olt. Mercury contamination of surface sediments in the Babeni reservoir (see Table 1) is too high with respect to sediment quality guidelines and is one order of magnitude higher than the local background concentrations measured in sediments from the upstream Vâlcea reservoir (Bravo *et al.*, 2009). An increase of mercury concentrations observed along the food chain lead to the highest values found in fish (Bravo *et al.*, 2014), 92 % of studied fish exceeded the threshold of 0.5 mg/kg w. w. with most of the mercury in the form of methylmercury.

3. 6 Khimprom, Kazakhstan

The Pavlodar Chemical Plant (Khimprom), is a former industrial factory that was designed as a dual-purpose production factory capable of manufacturing both agents of chemical warfare and civilian chemicals, including chlor-alkali plant which operated for 18 years and caused serious widespread contamination. The chlor-alkali plant is located 2 km south of Lake Balkyldak (15 km^2) and 5 km east of the River Irtysh. The most contaminated lake was Lake Balkyldak. It is a waste-water settling pond without outlet (Ullrich *et al.*, 2007) and in comparison with other aquatic ecosystems contaminated by mercury from chlor-alkali plant, Lake Balkyldak could be the most severely impacted lake ecosystem known to date and it is in need of remediation, since it represents a threat (Ullrich *et al.*, 2007). Sediments from Lake Balkydak are heavily contaminated with mercury (see Table 1) (Ullrich *et al.*, 2007) and it is used regularly by fishermen who catch fish both for their own consumption and for sale.

3.7 Karbid, Kazakhstan

The Plant of Synthetic Rubber or the "Karbid" is a chemical factory in central North Kazakhstan, which has been producing synthetic rubber while using mercury sulphate as a catalyst for almost 50 years. The entire industrial area is located on the west bank of the Samarkand Reservoir on the Nura River, near Temirtau in Karaganda Region. Even after decontamination of the site in 2013, high concentrations of mercury in sediments were detected at many sampling locations, with the highest being 174 mg/kg (Šír and Petrlík, 2015), even 70 km from the source (See Table1).

3.8 Vlora, Albania

North of Vlora in Albania is the site of a former chemical manufacturing complex consisting of a chlor-alkali plant and plants for the production of VCM and PVC plastic, identified as "hot-spot" for mercury pollution in 2002 (Lazo and Reif, 2013), especially electrolysis and polymerisation plants. The former chemical factory is located near the Vlora Bay, a part of the Adriatic Sea. There is another area used as dump for disposal of contaminated sludge between the former chemical factory and the coast with concentrations from 0.33 to 156 mg/kg (Beqiraj, Cullaj and Kotorri, 2008). As a result of spreading contamination from the former chemical complex, high concentrations of mercury were found in sediments, seawater and biota in the area near the former factory (Lazo and Reif, 2013).

Chemical factory	locality	mg/kg	notes	Reference
Spolchemie in Ústí nad Labem	River Bílina	32	6.7 mg/kg in biofilm	(Pokorný *et al.*, 2011)
Marktredwitz Chemical Factory	Kössein water stream	269	maximum, ethyl-mercury + methyl-mercury	
	River Reslava	435	highest concentration from 1983	
	Skalka Reservoir	12.9	456,000 m3 of sediment	(Titl *et al.*, 2011)
Fortischem in Nováky	discharge to River Nitra	131	112 µg/l in wastewater	
Fortischem in Nováky	lagoon	197		(Labunská, 2002)
Oltchim in Râmnicu Vâlcea	Babeni Reservoir	0.8 - 6.6	5,8 mg/l in surface water	
Chemical Complex in Pavlodar	Lake Balkyldak	1500	*first 9 km	
Karbid in Temirtau	River Nura	150-240	in 25 km after discharge	

Table 1: Mercury concentration in sediments in water bodies around chemical plants

4 Results

Results of the analyses of mercury in fish in the vicinity, mostly downstream from the described factories/contaminated sites are summarized in graph at Figure 3.
Mercury analysis come either from the research by IPEN and Arnika in 2012 (Arnika Association and IPEN Heavy Metals Working Group, 2013) or from other studies published in accessible literature (Andreji *et al.*, 2005; Maršálek *et al.*, 2005; Žlábek *et al.*, 2005; Bravo *et al.*, 2010; Corsi *et al.*, 2011; Musil *et al.*, 2015; Šír and Petrlík, 2015) between the years 2005 and 2015. Part of these results were also included and discussed in the global-scale assessment of mercury in fish (Evers *et al.*, 2014; Buck *et al.*, 2019).

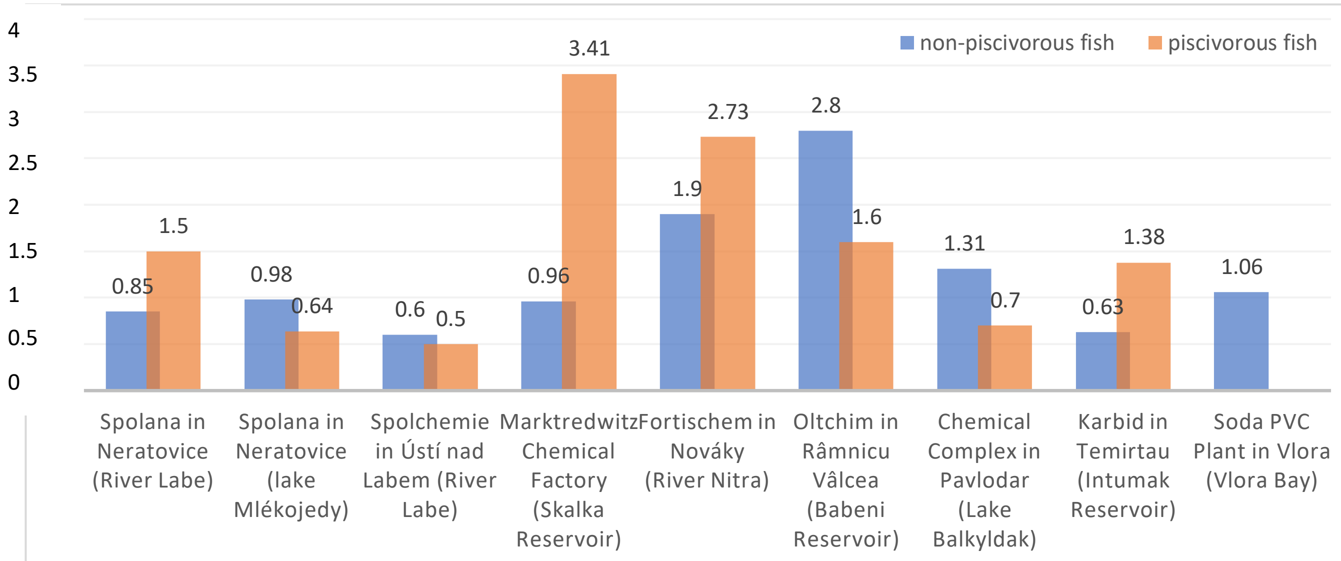

Figure 3: Mean levels of mercury in muscle of fish on contaminated sites (mg/kg wet weight)

Mercury levels were in the range of 0.5 – 3.41 mg/kg. The threshold of 0.5 mg/kg w.w. established by the WHO (WHO, 2004) was exceeded in all fish samples presented in this study but the sample downstream of Spolchemie which is discussed further below.

Mercury levels in fish were highly elevated in compared to the natural level of mercury, nevertheless directly downstream of Spolchemie mean mercury concentrations in fish did not exceed the threshold of 0.5 mg/kg w.w. established by the WHO (WHO, 2004), but Žlábek *et al.* (2005) found that mean mercury levels in common bream (Abramis brama) from the River Labe 20 km downstream from the Spolchemie exceeded WHO limit. Randak *et al.* (2009) found that the mean mercury concentration in chub (Leuciscus cephalus L.) caught downstream of the factory was 0.26 mg/kg w.w. A similar mean value of 0.28 mg/kg w.w. was found in the investigation by the Arnika Association and IPEN in 2012 in common bream muscle (Abramis brama2012 (Arnika Association and IPEN Heavy Metals Working Group, 2013). If the stricter US EPA (US EPA 2001) reference dose of 0.22 mg/kg is used, eating fish from the River Labe downstream from the confluence with the River Bílina poses a health risk.

The most considerable were mercury levels in fish also in Vlora, because the bay is important fishing area. The study made by the Arnika Association, Eden Center and IPEN in 2013 reported that a mean mercury concentration in mullet (Mullus surmuletus) was 0.617 mg/kg w.w. (Eden Center, Arnika Association, IPEN, 2013) and a majority of mullets exceeded current human health criteria for mercury established by the WHO (WHO, 2004) and was nearly three times higher than the EPA (US EPA, 2001) reference dose of 0.22 mg/kg. High levels of mercury have also been found in the red mullet muscle (Mullus barbatus) - 1.06 mg/kg d. m. (Corsi *et al.*, 2011) or 0.14 – 3.39 ppm in small sharks (Galeus melastomus) of the Adriatic Sea (Storelli, Ceci and Marcotrigiano, 1998).

5 Discussion

In most cases fish caught downstream from described sites contaminated in result of long lasting use of mercury in chemical factories had levels of mercury which exceeded current human health criteria for mercury established by the WHO (WHO, 2004), see graph at Figure 3. This contamination can last even after major part of contamination is remediated as it was documented in fish caught downstream from Marktredwitz in the Czech dam near German borders. Remaining contamination in Nura River downstream from decontaminated area in Temirtau is a similar case. Problem is in remaining contamination in sediments which were not remediated.

There was also observed simultaneous contamination with persistent organic pollutants (POPs) in some of here demonstrated cases. There is problem with contamination with polychlorinated dinbenzo-p-dioxins and dibenzofurans (PCDD/Fs) which were unintentional by-products mainly in residues from production of chlorine by using graphite electrodes in chlor-alkali plants (UNEP, 2013). High levels of PCBs were measured in sediments from Nura River (Petrlik *et al.*, 2015). These may result form the use of chlorinated paraffins as flame retardants in rubber (UNEP, 2013) but most likely leaked from metallurgical plants located in Termitau as well.

There is also high contamination of water sediments and fish with other POPs such as hexachlorocyclohexanes (HCHs) and/or hexachlorobenzene (HCB) in the vicinity of Vlora in Albania or downstream from Spolchemie in Usti and Labem, Czech Republic. This was caused by production of pesticides in chlorine chemical factories in the past (Vlora, Spolana Neratovice, Spolchemie Usti and Labem and others) and/or by releases of HCB as unintentional by-product from production of chlorinated solvents (Spolchemie Usti nad Labem).

Described cases demonstrate how complex contamination inside the chemical factories as well as in the sediments outside of their former production areas can be.

IPEN developed basic guidance for identification, management and remediation of mercury contaminated sites in order to assist mainly to developing countries or countries with economies in transition in finding solutions for such sites as they are described in our study (Bell, 2016). Its previous version included basic technologies to address also POPs contaminated sites as well. IPEN document became basis for development of guidance adopted by the Conference of Parties (COP) to the Minamata Convention later on (Minamata Convention on Mercury, 2019). This document as well as Technical Guidelines for mercury waste (Basel Convention, 2015) does not suggest waste incineration as environmentally sound management for treatment of wastes containing mercury because of uncontrolled releases of mercury. This suggestion is fully reflected also in BAT/BEP Guidelines for waste incineration developed within framework of the Minamata Convention ('Guidance on best available techniques and best environmental practices (Minamata Convention on Mercury) - Waste Incineration Facilities', 2016). Indirect thermal desorption seems to be most suitable way for evaporation of both mercury and POPs from contaminated material from sites described in cases of contaminated sites originated from chemical production described in this study. POPs can be destroyed by non-combustion technologies in residues from remediation of the sites described in this study (Bell, 2020).

Some of the sites described in our study were already fully and/or partly remediated. Remediation of the sediments from the vicinity of Nura River downstream for Temirtau is described in one of previous studies. However high levels of mercury and PCBs in sediments and continuing contamination of fish downstream from the contaminated site were observed. Former pesticide factory in Marktredwitz was also remediated but high levels of mercury in sediments downstream remained as reservoir of continuing mercury pollution for river flowing into Skalka reservoir in the Czech Republic where methylation leads to high levels of mercury in fish.

6 Conclusions

Mercury contamination of fish downstream from contaminated sites with origin in the past chemical production and/or abandoned technologies represent serious risks for human health and represents also serious environmental threat to water ecosystems.

Contamination of former chemical plants areas and their vicinity is very complex and needs to be addressed by combination of remediation techniques. This problem was addressed in various guidance documents prepared within the framework of both Basel and Minamata Conventions, and in more details also in IPEN studies and guidance documents.

7 Acknowledgements

The study was financially supported by the Government of Sweden through IPEN, the Global Greengrants Fund, and the Sigrid Rausing Trust.

8 References

Andreji, J. *et al.* (2005) 'Concentration of Selected Metals in Muscle of Various Fish Species', *Journal of Environmental Science and Health, Part A,* 40(4), pp. 899–912. Available at: https://doi.org/10.1081/ESE-200048297.

Arnika Association and IPEN Heavy Metals Working Group (2013) *Chlor-alkali plants: Neratovice, Ústí nad Labem and Some Other Chemical Hot Spots in the Czech Republic.* Arnika - Toxics and Waster Programme and IPEN, p. 9.

Basel Convention (2015) *General technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants*. Geneva.

Bell, L. (2016) 'Guidance on the identification, management and remediation of mercury-contaminated sites'. IPEN.

Bell, L. (2020) 'NON-Combustion Technology for POPs waste destruction: Replacing incineration with clean technology'. Gothenburg - Perth.

Beqiraj, A., Cullaj, A. and Kotorri, P. (2008) 'High-contaminated soil with mercury in Bay of Vlora (Albania) and its possible remediation'.

Bravo, A.G. *et al.* (2009) 'Historical record of mercury contamination in sediments from the Babeni Reservoir in the Olt River, Romania', *Environmental Science and Pollution Research,* 16(1), pp. 66–75. Available at: https://doi.org/10.1007/s11356-008-0057-5.

Bravo, A.G. *et al.* (2010) 'Mercury human exposure through fish consumption in a reservoir contaminated by a

chlor-alkali plant: Babeni reservoir (Romania)', *Environmental Science and Pollution Research*, 17(8), pp. 1422–1432. Available at: https://doi.org/10.1007/s11356-010-0328-9.
Bravo, A.G. *et al.* (2014) 'Extremely elevated methyl mercury levels in water, sediment and organisms in a Romanian reservoir affected by release of mercury from a chlor-alkali plant', *Water Research*, 49, pp. 391–405. Available at: https://doi.org/10.1016/j.watres.2013.10.024.
Buck, D.G. *et al.* (2019) 'A global-scale assessment of fish mercury concentrations and the identification of biological hotspots', *Science of the total environment*, 687, pp. 956–966.
Corsi, I. *et al.* (2011) 'Ecotoxicological Assessment of Vlora Bay (Albania) by a Biomonitoring Study Using an Integrated Approach of Sublethal Toxicological Effects and Contaminant Levels in Bioindicator Species', *Journal of Coastal Research*, (58), pp. 116–120. Available at: https://doi.org/10.2112/SI_58_11.
Eden Center, Arnika Association, IPEN (2013) 'Contaminated site: Vlora Mercury Hot Spot in Albania.' Arnika - Toxics and Waster Programme and IPEN.
Evers, D. *et al.* (2014) 'Global mercury hotspots: New evidence reveals mercury contamination regularly exceeds health advisory levels in humans and fish worldwide', *BRI-IPEN Science Communications Series*, 34, p. 2014.
Greenpeace Czech Republic (2002) *Greenpeace evidences huge mercury contamination of the Spolana*. Press release by Greenpeace Czech Republic from 16th of July 2002.
'Guidance on best available techniques and best environmental practices (Minamata Convention on Mercury) - Waste Incineration Facilities' (2016). Geneva, UNEP.
Labunská, I. (2002) 'The Nováky Chemical Plant (Novácké chemické závody) as a source of mercury and organochlorine contaminants to the Nitra River, Slovakia.' Greenpeace Research Laboratories.
Lazo, P. and Reif, J. (2013) 'Vlora, an Abandoned PVC Factory at the Mediterranean Coast: Mercury Pollution, Threat to Humans, and Treatment Options', *Bioremediation of mercury: current research and industrial applications*, pp. 67–80.
Maršálek, P. *et al.* (2005) 'Mercury and Methyl-mercury Contamination of Fish from the Skalka Reservoir: A Case Study.', *Acta Veterinaria Brno*, (74), pp. 427–434.
Minamata Convention on Mercury (2019) 'Guidance on the management of contaminated sites.' UNEP/MC/COP.3/8/Rev.1, Geneva, UNEP.
Musil, J. *et al.* (2015) 'Realisation of fish muscles analysis including their fish out from the River Labe and the Mlékojedy pond.' T. G. Masaryk Water Research Institute Praha.
Petrlik, J. *et al.* (2015) 'Contaminated sites and their management. Case studies: Kazakhstan and Armenia.' Arnika - Toxics and Waste Programme, AWHHE, CINEST, EcoMuseum.
Pokorný, D. *et al.* (2011) 'Report on Water Management in the Czech Republic in 2010.' Report of Department of State Administration of Water Management and River Basin Ministry of Agriculture of the Czech Republic and Department of Water Protection of the Czech Republic Ministry of the Environment of the Czech Republic.
Randak, T. *et al.* (2009) 'Effects of pollution on chub in the River Elbe, Czech Republic', *Ecotoxicology and Environmental Safety*, 72(3), pp. 737–746. Available at: https://doi.org/10.1016/j.ecoenv.2008.09.020.
Šír, M. and Petrlík, J. (2015) 'Results of environmental sampling in Kazakhstan: mercury, methylmercury, PCBs and OCPs contamination of the River Nura (Final report). Contaminated sites and their management. Case studies: Kazakhstan and Armenia.' Arnika - Toxics and Waste Programme.
Storelli, M., Ceci, E. and Marcotrigiano, G. (1998) 'Comparative study of heavy metal residues in some tissues of the fish Galeus melastomus caught along the Italian and Albanian coasts', *Rapp. Comm. Int. Mer. Medit*, 35, pp. 288–289.
Titl, F. *et al.* (2011) 'Mercury on the Tributary to the Skalka Dam. Assessment and Proposed Measures. A Feasibility Study.' Aquatest a. s.
Ullrich, S.M. *et al.* (2007) 'Mercury contamination in the vicinity of a derelict chlor-alkali plant. Part I: Sediment and water contamination of Lake Balkyldak and the River Irtysh', *Science of The Total Environment*, 381(1), pp. 1–16. Available at: https://doi.org/10.1016/j.scitotenv.2007.02.033.
UNEP (2013) 'Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport.' UNEP Chemicals Branch, Geneva, Switzerland.
US EPA (2001) 'Water Quality Criterion for the Protection of Human Health: Methyl- mercury.' Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency Washington, DC,.
WHO (2004) 'Safety evaluation of certain food additives and contaminants Food Additive series 52'. World Health Organization, international programme on chemical safety. Available at: http://apps.who.int/iris/bitstream/handle/10665/43038/924166052X.pdf;jsessionid=6E5829865EEC24EE3D6D7580992C27AB?sequence=1.
Žlábek, V. *et al.* (2005) 'Mercury content in the muscle of fish from the Elbe River and its tributaries', *Czech Journal of Animal Science*, 50(11), pp. 528–534. Available at: https://doi.org/10.17221/4258-CJAS.