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MERCURY IN AQUATIC SEDIMENTS AND SOILS FROM CROATIA

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Mercury is one of the most toxic and hazardous pollutant which occurs in the environment in different chemical forms, of which methylmercury is the most dangerous. Recently it was recognised that long-term anthropogenic inputs of mercury into environment resulted in the global mercury pollution and it was concluded that action should be taken to quantify the pollution sources and reduce human-generated releases of mercury. This paper presents new data on mercury levels in aquatic sediments from about 15 Croatian rivers, lakes and estuaries. It also brings data on mercury concentrations in soils from eight different regions of Croatia. Distribution of mercury species is discussed in more details for the Sava River, the Krka estuary and the Kaštela Bay on the eastern Adriatic coast. Results show that sediments and soils from Croatia are generally not contaminated by mercury, except for some rivers and coastal locations under direct anthropogenic influence.

KEY WORDS: *environment, methylmercury, pollution*

It has recently been established that mercury levels have increased considerably since the onset of the industrial age. The United Nations Environment Programme (UNEP) Governing Council concluded in 2003 that there was sufficient evidence of significant global adverse impact from mercury to warrant further international action to reduce the risks to humans and wildlife from release of mercury into the environment. It was decided that national, regional and global actions should be initiated, and the Mercury Programme (1) was established within the UNEP Chemicals. This programme includes Croatia. One of the important goals of this programme is to determine the degree of environmental contamination by mercury and identify the hot spots and populations at risks.

Mercury is released into the environment from natural and anthropogenic sources (such as fossil fuels, mining activities, waste disposal of mercury-containing products, use of mercury in gold mining, and chlorine-alkali production) and has affected

the biogeochemical cycle, which has in turn led to mercury transport at long distances from the source, as well as to its efficient recycling between different environmental compartments (2). Mercury undergoes chemical transformations in the environment and can be changed from inorganic species (primarily by microbiological processes) into methylmercury, which has the capacity to accumulate in living organisms (bioaccumulation) and to concentrate up the food chain (biomagnification), especially in the aquatic one. It is therefore of the greatest concern, as nearly all of the mercury in fish is methylmercury. Methylmercury is the most toxic mercury compound; it is a neurotoxicant that can readily pass the placental and the blood-brain barrier. Populations especially susceptible to mercury exposure are pregnant women (foetuses) and young children, because of the sensitivity of the developing brain. On the basis of risk assessment of populations at risks, a provisional tolerable weekly intake (PTWI) has been established

by the World Health Organization (WHO), which recommended dietary limits for methylmercury of $3.3 \mu\text{g kg}^{-1}$ of body weight per week. This limit was reviewed recently and a reduction recommended to $1.6 \mu\text{g}$ per kg^{-1} of body weight per week in order to protect the developing foetus (3). As the main route of exposure to methylmercury is the consumption of fish, most countries, including Croatia have regulated the maximum allowed level of mercury in the form of methylmercury in fish (4).

It is of great importance to assess mercury contamination of environments in Croatia. As methylmercury is mainly found in aquatic sediments (5), and then biomagnified in fish, it is important to identify the level of mercury in freshwater and marine sediments. In this work new data on mercury concentrations in sediments from Croatian rivers and east Adriatic coastal sediments will be presented and compiled with available literature data on mercury level in fish. In addition, some new data on mercury level in soils from various parts of Croatia will also be presented.

STUDY DESIGN AND METHODS

Study areas and sampling

In 2003-2005, freshwater sediments were collected from about 15 rivers, lakes and estuaries (Plitvice Lakes, the rivers Sunja, Pakra, Una, Korana, Blinja, Petrinjčica, Glina, Žirovnica, Mrežnica, Odra, Kupa, Sava, and the Krka River estuary) from the continental and coastal Croatia. A more detailed study of mercury distribution in sediments was performed in the Sava River and in the Krka River estuary. Coastal sediments were collected in the Kaštela Bay, which is situated in the central Croatian Adriatic, from 2000 to 2001. Soil samples were collected in 2003-2005 in eight Croatian regions: Banovina, Pokuplje, Eastern Lika, Posavina, Western Slavonija, Osijek area, Vukovar area and Šibenik area. Samples of aquatic sediments and soils were collected

within the project "Mitigation of Environmental Consequences of the War in Croatia - Risk Assessment of Hazardous Chemical Contamination". Sediments from the Krka River estuary were collected as a part of a Ph.D. thesis of *Cukrov* (6) and from the Kaštela Bay as a part of a Ph.D. thesis of *Foucher* (7).

Preparation of samples and analytical methods

Sediments were air dried under laminar flow, sieved and their fine fraction ($<63 \mu\text{m}$) separated for analysis. Soil samples were also air dried under laminar flow and their fraction $<2\text{mm}$ separated for analysis by sieving. This fraction was further ground to obtain a fine homogenous material for analysis. Total mercury (Hg) was measured in undigested sediments and soils using an AMA solid mercury analyser (LECO). For mercury determination in the coastal sediments, a portion of sediment was digested with HNO_3 and mercury was detected using the cold vapour atomic fluorescence spectroscopy (CV AFS, PSA) (7, 8). Methylmercury (MeHg) in sediment was determined using gas chromatography CV AFS after extraction to dichloromethane, ethylation and pre-concentration on a Tenax column (7). For quality control of Hg determination we used the following certified reference materials (CRM): estuarine sediment IAEA 405, marine sediment MESS-3 (NRC), freshwater sediment GBW 07311, and soil GBW 07410. CRM IAEA 405 was also used for quality control of MeHg determination. The results of CRM analysis are given in Table 1.

RESULTS AND DISCUSSION

Mercury in freshwater and estuarine sediments

On Figure 1 arithmetic means and standard deviations of Hg concentrations in sediments from Croatian rivers, lakes and estuaries are presented. Maximum acceptable mercury concentrations are defined for different environmental media from which mercury may be introduced to humans, such

Table 1 Total mercury and methylmercury findings in certified reference materials (CRM)

CRM	Found value / mg kg^{-1} $\bar{X} \pm \text{SD}$	Certified value / mg kg^{-1} $\bar{X} \pm \text{SD}$
Soil - GBW 07410 (Hg)	0.085 ± 0.025	0.066 ± 0.025
Sed. - GBW 07311 (Hg)	0.071 ± 0.010	0.072 ± 0.028
Sed. - MESS-3 (Hg)	0.117 ± 0.020	0.091 ± 0.009
Sed. - IAEA-405 (Hg)	0.87 ± 0.04	0.81 ± 0.14
Sed. - IAEA-405 (MeHg)	0.0052 ± 0.0007	0.00549 ± 0.00053

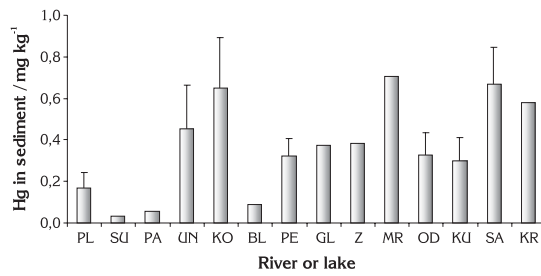


Figure 1 Total mercury mass fractions ($\bar{X} \pm SD$) in aquatic sediments from Croatian rivers, lakes and estuaries (PL- Plitvice Lakes, SU-Sunja, PA-Pakra, U-Una, KO-Korana, BL-Blinja, PE-Petrinjska, GL-Glina, Z-Žirovnica, MR-Mrežnica, OD-Odra, KU-Kupa, SA-Sava, KR-Krka estuary)

as drinking water, freshwater, air, soil and food (Table 2). However, maximum allowed concentrations of metals are usually not defined for aquatic sediments and different methods have to be used to evaluate the degree of contamination of aquatic sediments. Some countries define recommended values for metals, which may help to evaluate the contamination level of aquatic sediments. For example, in Norway sediments are divided in five quality categories (from good to bad) according to mercury mass fraction in mg kg^{-1} : I (<0.1); II (0.1 to 0.6); III (0.6 to 3); IV (3 to 5) and V (>5). The same threshold of 0.1 mg kg^{-1} is given by the French Agency for Water (7) to define whether sediments are contaminated with mercury or not. According to these criteria, only a few small rivers (the Sunja, the Pakra, and the Blinja) and most samples from Plitvice Lakes are not contaminated by mercury. Most analysed sediments were only

slightly contaminated (taken from the rivers Una, Petrinja, Glina, Žirovnica, Odra, Kupa, and Krka), whereas in some rivers (the Korana, the Mrežnica, and the Sava) mercury exceeded the 0.6 mg kg^{-1} threshold and these sediments can be classified as contaminated by mercury. Our findings indicate that most of the examined rivers are exposed to a general anthropogenic contamination (mercury introduced by inputs of untreated municipal and industrial wastewaters and dry and wet deposition from the atmosphere), whereas for only few rivers local sources of mercury are suspected. As the number of samples taken during this screening of sediments from Croatian rivers (for some rivers only one sediment sample was analysed) is limited, definite conclusions on mercury contamination levels will have to wait for a further, more detailed research.

Distribution of mercury was studied in more detail in sediments of the Sava River (Figure 2) on the transect from Jesenice in Slovenia to Lukavec in Croatia, which extends over almost 300 km. Results demonstrated that Hg mass fraction all along the studied transect was relatively high [(0.4 to 1.0 mg kg^{-1}), and that the impact of untreated wastewaters from Zagreb (which are discarded into the Sava River between Oborovo and Martinska Ves) could not be determined. According to some authors (14, 15), elevated mass fraction of mercury in the Sava River sediments are partly the consequence of a geological anomaly, that is, a natural mercury enrichment of the upstream Slovenian drainage basins. The same authors found a 100-fold Hg enrichment in deep overbank sediments, as compared to the surface sediment, and attributed this to an even higher Hg input from the Slovenian catchment area in the past. Literature data on mercury levels in fish from the Sava River (16) did not show any difference between fish caught upstream and downstream of Zagreb, which is in accordance with the uniform level of mercury in sediment. Mercury levels in fish from the Sava were 2-5 times higher

Table 2 Maximum allowed levels of total mercury and methylmercury in various environmental media in Croatia

Environmental media	Maximum allowed level	Reference
Drinking water	$1 \mu\text{g L}^{-1}$	9
Freshwater		
Class I-II	$(0.005 \text{ to } 0.020) \mu\text{g L}^{-1}$	10
Class III-IV	$(0.02 \text{ to } 1.0) \mu\text{g L}^{-1}$	
Seawater		
Class 1	$(0.005 \text{ to } 0.02) \mu\text{g L}^{-1}$	10
Class 2	$(0.02 \text{ to } 0.3) \mu\text{g L}^{-1}$	
Soil (agricultural)		
Humus poor soils	1.0 mg kg^{-1}	11
Humus rich soils	2.0 mg kg^{-1}	
Air		
Limit value (indoors)	$1 \mu\text{g m}^{-3}$	12
Recommended value	$0.01 \mu\text{g m}^{-3}$	
Fish		
Predatory fish (tuna), mollusk, crustaceans	Hg : 1.0 mg kg^{-1} MeHg : 0.8 mg kg^{-1}	4
All other fish	Hg : 0.5 mg kg^{-1} MeHg : 0.4 mg kg^{-1}	

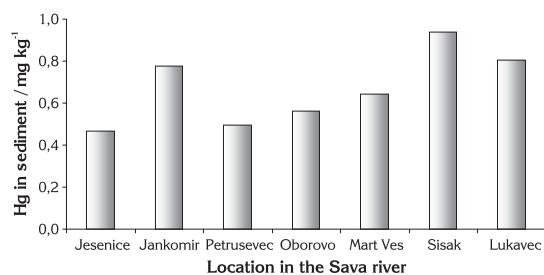


Figure 2 Total mercury mass fractions in sediments of the Sava River on the transect from Jesenice to Lukavec

than in fish from Lake Jarun. In some fish the mercury level was higher than the maximum allowed level of 0.5 mg kg^{-1} . Therefore, the Sava can be considered contaminated by mercury which originates from mixed geogenic and anthropogenic sources. Literature data on mercury levels in sediments of the Kupa River ($\text{Hg} < 0.2 \text{ mg kg}^{-1}$, ref. 17) were in good agreement with our measurements.

Distribution of mercury was also studied in the Krka River estuary (Figure 3). The horizontal profile of mercury in surface sediments, starting from the river toward the sea, showed that its mass fraction gradually increased from a very low value in Skradin to levels higher than 1 mg kg^{-1} in Šibenik (locations K6, M), reaching 3 mg kg^{-1} in Šibenik's port (locations L1, L2). These results suggest that the Krka River is not contaminated with mercury, but that there are important mercury contamination sources in the middle section of the estuary. Untreated municipal wastewaters of the town of Šibenik, which had for decades been discharged directly into the middle section of the estuary, certainly are an important source of mercury contamination. In addition, it was recently demonstrated (18, 19) that the transshipment terminal for the phosphate ores in Šibenik Port was the local source of contamination for numerous metals, including mercury. The Krka River estuary is an example of how long-term uncontrolled anthropogenic activities can cause local contamination of aquatic systems, which is recorded in bottom sediments.

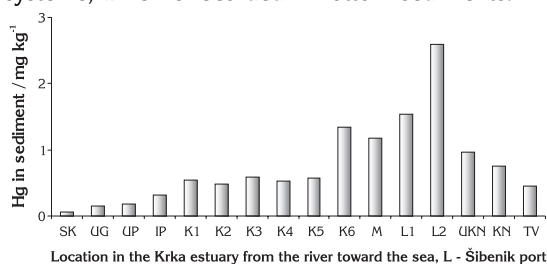


Figure 3 Total mercury mass fractions in sediments from the Krka River estuary (locations from Skradin (SK) to the exit from the Šibenik Channel (TV); L1 & L2 – Šibenik Port)

Mercury and methylmercury in coastal sediments

There are a number of papers dealing with the level of mercury in sediments along the eastern Adriatic coast (Table 3). They show that mercury in these sediments is generally low, but that it increases in larger towns such as Šibenik and Dubrovnik (20). A mercury contamination hot spot (and probably for some other pollutants too) is the Kaštela Bay with its heavy industry. The main source of mercury in

Table 3 Literature data on total mercury and methylmercury levels in coastal sediments of the eastern Adriatic

Location	Hg / mg kg^{-1} (ref)	MeHg / mg kg^{-1} (ref)
North Adriatic	0.11 to 0.43 (20)	-
Krka river	0.17 to 0.43 (20, 21)	0.002 to 0.003 (21)
estuary	0.68 (20)	
Šibenik port		
Kornati archipelago	0.24 to 0.42 (20)	-
Dubrovnik area	0.14 to 0.56 (20)	-
Dubrovnik port	1.45 (20)	
Kaštela bay	0.07 to 4.39 (22)	-
	0.64 to 10.11 (23)	0.002 to 0.02 (23, 24)
	17 to 74 (25)	0.006 to 0.037 (25)
	3.8 to 64.8 (7)	0.004 to 0.064 (7)

this area was a chlorine-alkali plant which operated for almost 40 years, discharging about 60 tonnes of elemental mercury into the bay (26). More than 20 years ago, it was shown that the sediments in front of the plant were heavily contaminated by mercury (22-24) and that methylation of mercury was taking place in these sediments. It was further demonstrated that mercury was spreading, which led to a steady increase in mercury levels in other parts of the bay (27). The most recent investigation (Figure 4) showed that sediments in front of the plant still contain extremely high mercury levels, and that methylation of mercury in these sediments is very intensive, resulting in methylmercury concentrations of up to 100 times higher than in uncontaminated sediments. A common level of methylmercury in uncontaminated aquatic sediments is about $1 \mu\text{g kg}^{-1}$ or lower (8, 21), whereas in the sediments of the Kaštela Bay these levels reached $60 \mu\text{g kg}^{-1}$ (7, 25). Contamination with mercury and high mass fractions of methylmercury were not limited only to the surface sediment, as very high levels of both species were detected up to a depth of 50 cm (Figure 4). Depth distribution of mercury was very irregular; two depth profiles in sediment cores sampled at a nearly same location illustrate this irregularity in Figure 4. This is a consequence of the anthropogenic disturbance of sediments in front of the chlorine-alkali plant. Parallel investigation of the depth distribution of radionuclides and mercury in these sediments verified that the sediments were actually a mixture of natural sediments and coal ash (from the plant's power production unit), rich in radionuclides, that was dumped into the sea on several occasions (28). This suggests that, even though the chlorine-alkali plant was shut down more than ten years ago, mercury deposited in sediments is still a hazard for

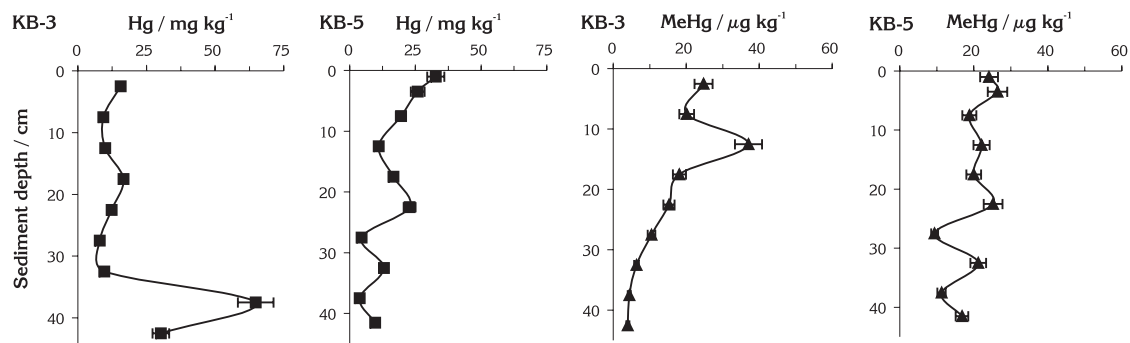


Figure 4 Depth distributions of total mercury and methylmercury in sediments from the Kaštela Bay, collected near chlorine-alkali plant (KB-3 and KB-5 cores were sampled at the same location, KB-3 in February 2001 and KB-5 in October 2001)

the whole bay, especially in view of biomagnification of methylmercury in local fish.

Several studies investigated mercury and methylmercury in fish in the Kaštela Bay and other parts of the Croatian Adriatic coast (Table 4). Higher levels of mercury and methylmercury in fish than permitted by Croatian regulations (Table 2) were determined in the fish from the Kaštela Bay, but also in marketed fish (24, 29). There are few reports on the dietary intake of mercury and methylmercury from seafood from the Adriatic coast (Table 4). Calculated dietary intakes were compared with the WHO PTWI for total mercury (300 μg Hg per person per week) and for methylmercury (200 μg Hg per person per week). The mean weekly mercury intake of the general population in Croatia, calculated on the basis of the mean annual fish consumption, is 19 μg of total mercury and 16 μg of methylmercury per person per week, which corresponded to less than 10 % of PTWI for both species (31). However, in coastal areas where more fish is consumed (Kaštela Bay, Vis) and where the level of mercury in fish was higher, the mean dietary intake was 10 times higher than in the general population (30). In the Kaštela Bay, 20 % of

subjects had dietary intake higher than PTWI for total mercury and 16 % for methylmercury. If we take into account the recently recommended lower PTWI values for methylmercury (3), the percentage of fishermen families in these areas whose intake exceeded PTWI for methylmercury would be even higher.

Mercury in soil

Figure 5 shows the average mass fractions of mercury in soils collected in eight Croatian regions. All values were lower than 1.0 mg kg^{-1} , which is the maximum allowed level for mercury in agricultural soils (Table 2). These soil samples, however, were collected close to the urban areas, and moderate contamination from the atmosphere could be expected. The highest values were found in Posavina, where soil samples were collected at same locations as the sediments of the Sava River. These higher values might also reflect the above mentioned geological anomaly related to the higher mercury load from the Slovenian part of the Sava River catchment (14, 15). A very high local contamination of soil by mercury was found only in one location in the town of Sisak (levels reaching 30 mg kg^{-1}), most probably due to the local heavy

Table 4 Literature data on total mercury and methylmercury levels in fish from the eastern Adriatic and calculated intake of mercury species from fish

Hg in fish / mg kg^{-1} (location)	MeHg in fish / mg kg^{-1} (location)	Fish consumption (g per week)	Intake of Hg from fish (μg per week)	Intake of MeHg from fish (μg per week)	Ref.
0.26 to 1.54 (KB)	0.12 to 1.45 (KB)	-	-	-	23, 24
0.11 to 2.27 (A)	0.11 to 2.13 (A)	-	-	-	29
0.05 to 0.63 (KB)	0.01 to 0.51 (KB)	991	194	146	30
0.01 to 0.65 (Vis)	0.01 to 0.50 (Vis)		(>PTWI: KB-20%, Vis-5%)*	(>PTWI: KB-16%, Vis-3%)**	
0.17±0.12 (A)	0.15±0.11	110	19	15	31
0.15 to 0.37 (A)	-	183	20 to 70	-	32, 33

KB – Kaštela bay; A-Adriatic (marketed fish);

*based on PTWI for Hg of 300 μg Hg per person per week;

**based on PTWI for MeHg of 200 μg MeHg per person per week

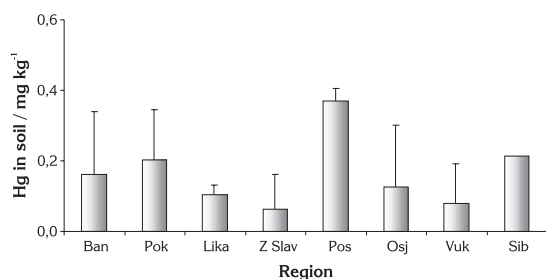


Figure 5 Total mercury mass fractions ($X \pm SD$) in soils from eight Croatian regions (Ban-Banovina, Pok-Pokuplje, Lika-Eastern Lika, Pos-Posavina, ZSlav-Western Slavonija, Osj-Osijek area, Vuk-Vukovar area, Sib-Sibenik area)

industry. In general we can conclude that the analysed soils were not contaminated by mercury.

CONCLUSIONS

The analyses of about 70 samples of aquatic sediments and about 100 samples of soils show that these types of environmental samples in Croatia are generally not contaminated by mercury. Increased levels of mercury were detected in sediments from some rivers (the Korana, the Mrežnica, and the Sava) and further research is needed to establish the sources and the extent of this contamination, as well as the levels of mercury in fish from these rivers. At some locations, mercury contamination was the consequence of local anthropogenic sources, for example in the middle section of the Krka River estuary. A hot spot was found in the soil at one location in the town of Sisak, which should probably need remediation. The most important mercury contamination hot spot is still the Kaštela Bay that had been polluted from the chlorine-alkali plant for years. Generally, a more systematic research of mercury levels in Croatian aquatic systems is needed, especially at locations where there are known sources of contamination, releasing raw municipal and industrial waste.

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Sažetak**ŽIVA U AKVATIČKIM SEDIMENTIMA I TLIMA U HRVATSKOJ**

Živa je jedan od najtoksičnijih i najopasnijih zagađivala okoliša. Specifične kemijske karakteristike žive uzrok su njezina vrlo kompleksnog biogeokemijskog ciklusa u okolišu, a pojedine specije tog elementa posjeduju vrlo visoku toksičnost. Anorganska živa se u vodenim sustavima metilira mikrobiološkim procesima, a nastala metil-živa akumulira se u vodenim organizmima. Prije nekoliko godina utvrđeno je da je došlo do globalnog zagađenja živom zbog dugotrajnog antropogenog unosa žive u okoliš, te je UNEP (engl. United Nations Environment Programme) pokrenuo internacionalni program s ciljem da se utvrde načini i količine unosa žive u okoliš djelovanjem čovjeka te predlože mjere da se taj unos smanji. U ovom radu prikazani su novi podaci o sadržaju žive u akvatičkim sedimentima i tlima u Hrvatskoj. Analizirani su sedimenti iz petnaestak rijeka, jezera i ušća te iz obalnih područja Jadrana, kao i tla iz osam različitih regija s područja cijele Hrvatske. Detaljnije je prikazana raspodjela kemijskih oblika žive u sedimentima rijeke Save, ušća rijeke Krke i Kaštelanskog zaljeva. Rezultati su pokazali da sedimenti i tla uglavnom nisu zagađeni živom, s izuzetkom nekoliko riječnih sustava koji su izloženi antropogenom utjecaju, te posebice Kaštelanskog zaljeva koji je zagađen živom podrijetlom iz tvornice klor-alkalija. Prikazani podatci upotpunjeni su dostupnim literaturnim podacima o razinama žive u okolišu u Hrvatskoj, posebice o masenim udjelima živinih spojeva u riječnim i morskim ribama, kao i procjenama unosa žive putem konzumacije riba u hrvatsku populaciju.

KLJUČNE RIJEČI: *metil-živa, okoliš, zagađenje*

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