Arh Hig Rada Toksikol 2001:52:229–237

CONFERENCE PAPER

LEAD, CADMIUM, AND MERCURY DIETARY INTAKE IN CROATIA

MAJA BLANUŠA AND DIANA JUREŠA

Institute for Medical Research and Occupational Health, Zagreb, Croatia

Received March 2001

This paper gives an overview of published data on levels of lead, cadmium, total and methyl-mercury in various food items, and of a daily dietary intake assessment in Croatia focusing on the last 10 years. It briefly describes the most reliable methods for quantitative analysis of lead, cadmium, and mercury in biological material. Lead and cadmium concentrations in vegetables and in organs of domestic animals refer to non-exposed rural areas. Mercury concentrations in fish and mussels refer to industrially polluted and non-polluted areas of the Adriatic. The daily dietary intake of lead and cadmium was assessed on the basis of duplicate-diet-collection and food-disappearance method. The assessment of the total and methyl-mercury dietary intake was based on dietary surveys of family seafood consumption. Lead and cadmium intake through food in the general population was 6–40% of the Provisional Tolerable Weekly Intake (PTWI), depending on the assessment method. The only Croatian population consuming more mercury through seafood is the one living in Dalmatia, approaching the PTWI defined by WHO.

Key words:
atomic absorption spectrometry, duplicate diet, fish, mussel, total and methyl-mercury, vegetable

The major route of exposure of general population to lead, cadmium, and mercury is through air and/or diet. The three metals are very toxic and their absorption and toxicity depends on dose and, among other diet constituents, on intake of essential metals through diet. Few literature data have been reported on the assessment of

Presented at the ICS-UNIDO Workshop on Contamination of Food and Agroproducts, 28 September – 1 October 2000, Varaždin, Croatia

dietary intake of lead, cadmium, or mercury in Croatia (1–4). More documented are the levels of toxic metals in various food items (1, 5–12). Most reports published by the Croatian Public Health Institutes relate to statistical evaluation of compliance of food control of toxicants with the Croatian legislation and not to the assessment of the normal population dietary intake of certain toxic metal pollutants.

This aim of this paper is to review literature data on the levels of lead, cadmium, and mercury measured in food items and on the daily dietary intake assessment in Croatia. Attention will be given to reports published in the last ten years.

METHODS

Most laboratories in Croatia use the atomic absorption spectrometry (AAS) method to analyse lead, cadmium, and mercury in food. The flame (F AAS) or the electrothermal method (ET AAS) are applied to analyse lead and cadmium and the cold vapour method (CV AAS) or the hydride generation method (HG AAS) to analyse mercury. When sampling individual food items to analyse metals (such as a vegetable), it is usually washed under the tap water, and the samples are cut to small pieces. Homogenisation is not necessary. The sampling of the duplicate or the market basket diets, however, requires homogenisation. One sample of duplicate diet contains food and drink consumed over 24 hours and collected from selected individuals. The market basket diet, also called total diet study, has the sample composed of 5–10 cooked or raw food items (13).

The destruction of the organic component of the sample depends on the method of analysis used and on the element analysed. To determine lead and cadmium by ET AAS dry ashing at 450 °C is the procedure of choice for the following reasons; at that temperature the two elements do not evaporate and ashes can be dissolved in a minimum quantity of concentrated HNO_3 and adjusted to a certain volume with deionised water to form the final 1% v/v HNO_3 solution. At this concentration of HNO_3 graphite tubes are lasting longer and the possibility to contaminate samples by large volumes of acid is smaller. Porcelain or glass crucibles should be avoided for dry ashing due to possible contamination with lead from crucibles or adsorption of lead on crucibles (14). Quartz or platinum crucibles are recommended instead.

For mercury analysis, nitric acid is successfully used in wet digestion to destroy biological materials and transform the organically bound mercury to the ionic form. This method involves heating of the sample in concentrated nitric acid up to 80 °C in a closed system. If the sample is heated in an open system, losses of mercury are inevitable (15). Another wet digestion method for mercury analysis involves addition of concentrated nitric acid and the sample treatment in a microwave oven. This method has some limitations when using the Teflon™ tubes, as these can be contaminated with mercury irreversibly. Even quartz tubes show occasional high blank values.

Distilled or suprapur HNO_3 and deionised water of 0.06 μS/cm conductivity should be used throughout the preparation phase. For the internal quality control of analysis during the analytical procedure it is also necessary to use a certified biological material (such as wheat flower, bovine liver, or fish muscle). National or international interlaboratory comparisons are recommended for the external quality control. In most references cited in this review the internal or external quality control procedures were not mentioned. The results in this report are expressed either as μg/kg wet weight of food item, μg/m^3 of air, μg/g of Hg in the hair or as μg/person of daily diet. All values are presented as mean ± standard deviation.

LEAD

The general population is exposed to lead through food, water, and air. Exposure to lead from the air is higher in urban population. Hazards from these sources have gradually diminished in Croatia due to removal of lead from gasoline. Measured concentrations of lead in the Zagreb air show a great decrease in average values over the last 10 years. Values dropped from 0.8 in 1990 to 0.09 μg/m^3 in 2000 (16, 17). The future population exposure to air lead is expected to fall further. However, concentrations of lead in different food items including vegetables are expected to remain at the present level if produced/grown in contaminated areas. Lead concentrations were measured in 81 samples of different kinds of brassicas collected in Zagreb household gardens in 1995–1996. A wide range of values was obtained from 19 to 1,871 μg Pb/kg wet weight with median value of 454 μg/kg (10). Vegetable samples (14 samples of carrot, 17 of parsley, 10 of lettuce, and 18 of potato) collected outside the Croatian capital and far from any possible pollution gave lead concentration values of 11.1±8.7 to 73.8±66.9 μg/kg (Figure 1, unpublished results obtained in our laboratory). Twen-

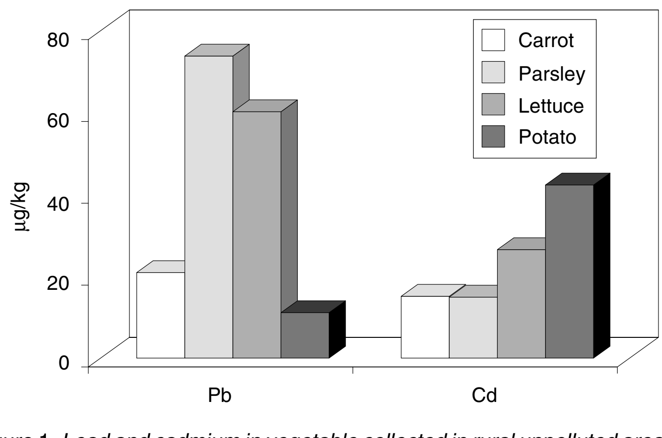

Figure 1 *Lead and cadmium in vegetable collected in rural unpolluted areas in Croatia (unpublished data; see text for details)*

ty-nine samples of the most commonly consumed Adriatic fish (Figure 2) were collected at the Zagreb market during in 2000. Lead concentrations obtained in the fish muscle ranged from 9.6 to 44.1 μg/kg wet weight (12). The concentration in the mussel tissue, however, was about 10 times higher, that is 121 to 150 μg/kg.

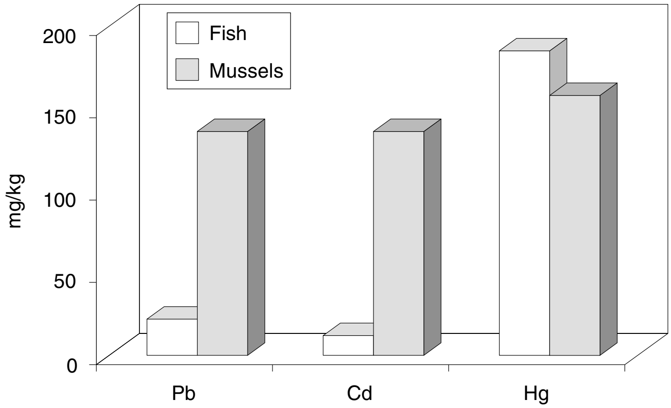

Figure 2 *Lead, cadmium and mercury in common fish and mussels from Adriatic Sea (unpublished data; see text for details)*

A study of daily dietary lead intake was performed during the 80s on a small group of women in Zagreb. The study was a part of a global-scale UNEP/WHO project (2, 18). After the international quality control of the analytical procedures, the results were compared between the participating countries. The method of duplicate diet collection and analysis of 119 samples showed that the daily dietary intake of lead in Zagreb was 15±7.2 μg/person (mean±SD). The findings in other countries varied between 26±7.9 μg/person in Stockholm and 46±18 μg/person in Beijing. Another study of daily dietary lead intake assessment in Croatia relied on lead levels in 19–22 foodstuffs. The composition of the diet and the consumption of the foodstuffs was calculated using the food-disappearance method, which relied on data published in the Statistical Yearbook of the Republic of Croatia. The daily dietary lead intake obtained by this method was 100 μg/person (4).

Absorption of lead from ingested food and water greatly depends on levels of other element present in the diet such calcium, iron, and zinc. It has been shown that dietary deficiencies in these essential elements enhance lead absorption (19). Therefore, when assessing toxic element daily intake of a certain population it is always useful to analyse the intake of other essential elements as well. During the UNEP/WHO project, zinc, copper, iron, manganese, and calcium were analysed in duplicate diets collected in Zagreb and compared to Swedish diets (Figure 3). All analysed elements in the Zagreb duplicate diets were lower than the Recommended Dietary Allowances (20) and significantly lower than in the Stockholm diets (21). The lower blood lead values found in the same study in the Stockholm population, as compared to Zagreb (18), might be partly associated with that difference in the daily intake of essential elements.

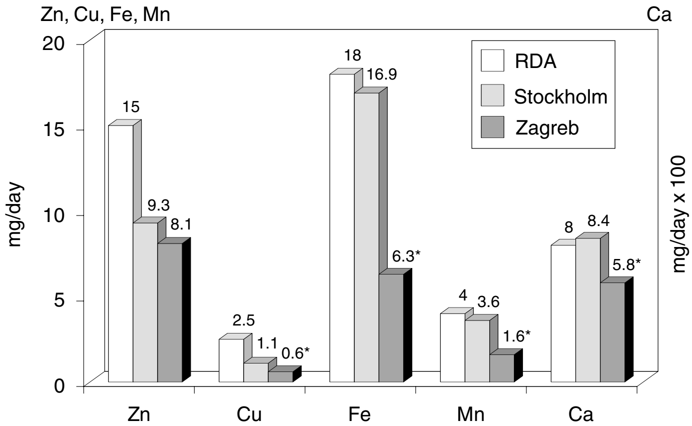

Figure 3 *Daily dietary intake of metals estimated by duplicate diet method (mg/person). *Statistical significant difference between Stockholm and Zagreb data tested by the Student's* t-*test. RDA= recommended daily allowance (adapted from ref. 21)*

Compared to the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (22), the daily dietary intake of lead found in the Croatian population of 232 μg/day and adult person makes only about 6–40% of PTWI, depending on the method applied.

CADMIUM

Cadmium is a nonessential, toxic metal to which humans are exposed through a variety of pathways including food, particularly leafy vegetables, grains, and cereals. The tobacco, itself a leafy plant, contains substantial amounts of cadmium, and its uptake is doubled in heavy smokers (19). Cadmium, which is in general lower in vegetables, muscle-meat, and fish, concentrates in shells and internal organs of different organisms. During the 80s cadmium was measured and reported in muscles, kidneys, and liver of several hundred samples taken from domestic animals (7). The range of cadmium concentrations in the muscles of cattle, pigs, lambs, fattened chicks, turkeys, and freshwater fish ranged from 17 to 102 μg/kg fresh weight. Cadmium in the liver of domestic animals was between 70 and 300 μg/kg and in the kidney from 150 to 650 μg/kg. The level of cadmium in common fish muscle from the Adriatic Sea was 5.1–49.1 μg/kg and in mussels from 130 to 142 μg/kg (Figure 2) (12). Vegetables (carrots, lettuces, and potatoes, 20 samples of each, unpublished results) collected in an non-polluted rural area in 1993–1995. contained 14.9±11.6 to 42.3±16.5 μg/kg wet weight of cadmium (Figure 1).

The UNEP/WHO study with duplicate diet collection showed a daily intake of 8.5±3.8 μg/person of cadmium (2). The other study performed using the food-disappearance method (4) reported the daily intake of 17.3 μg/person. These dietary daily cadmium intake assessments make about 20% of the PTWI (22) which is 65 μg/day and person.

MERCURY

Mercury in the form of methyl-mercury has the highest concentrations in seafood. It is concentrated from the sea with a concentration factor 10^4 to 10^5 (23). It is also considered methylated by micro-organisms in sediments and in marine organisms. Mercury accumulated in the tissues of fish usually takes the form of methyl-mercury (24). It is more toxic than the inorganic form and the population living near the coast and on the islands runs a greater risk of ingesting this highly toxic substance. However, the toxicity of methyl-mercury is moderated by the presence of selenium in fish (19). It has been found that the molar ratio between methyl-mercury and selenium in fish is 0.2–0.4 (25). Due to higher consumption of seafood, mercury monitoring of the Adriatic fish was of special interest for Croatia, as well as the mercury exposure assessment of general population in Dalmatia. Particular attention was paid to the central part of the Adriatic coast which was contaminated by mercury by a chlor-alkali plant. The earliest report on methyl-mercury concentrations in the sediment, mussel, and fish in the polluted area of the Kaštela Bay in the Central Adriatic was given by *Mikac and Picer* (26). They found 2–20 μg/kg of methyl-mercury in the sediment, 10–110 μg/kg in mussels (*Mytilus galloprovincialis*), and 102–1,448 μg/kg in various species of fish. The same area polluted with mercury from a chlor-alkali plant was further studied by scientists from the Institute of Oceanography and Fisheries in Split (8, 9, 25, 27, 28). The values of total mercury mass fractions in the contaminated area ranged from 162±5 to 1,230±70 and in the non-contaminated area from 83±6 to 380±8 μg/kg. Methyl-mercury participated with 70–97% of total mercury in fish (9). Mussels and oysters from the North Adriatic (*Mytilus galloprovincialis Lam*. and *Ostrea edulis L.*) were studied for methyl and total mercury content in different seasons by *Najdek and Sapunar* (6). Methyl-mercury varied from 36.5 to 298.9 μg/kg and total mercury from 58.3–766 μg/kg. The total and methyl-mercury content increased in correlation with the body mass. The mercury content in mussels and the most commonly consumed fish from different uncontaminated areas of the North and Middle Adriatic Sea purchased at the Zagreb market ranged from 142 to 252 μg/kg (Figure 2) (12).

The only report of mean weekly mercury intake of general population in Croatia calculated on the basis of mean annual fish consumption was evaluated by *Bošnir and co-workers* (11). Their calculation gave 19 μg of total mercury and 16 μg of methyl-mercury consumed per person and a week. It amounts to only 6–7% of PTWI (22) for the total and methyl-mercury. However, the population of the Adriatic coast and islands consuming 4–5 times more fish a week is likely to have a much higher total and methyl-mercury intake. *Buzina and co-workers* compared the total and methyl-mercury content of seafood and dietary intake in polluted and control areas of the Adriatic (1). The daily intake was evaluated on the basis of dietary surveys of family seafood consumption. The results were compared with PTWI for the total mercury (300 μg Hg per person) and for methyl-mercury (200 μg Hg per person). The respective percentages of subjects from the industrially polluted area whose dietary intake exceeded PTWI was about 20% for the total mercury and 16% for methyl-mercury. In the control area, about 5% of adult male population consumed more than the total mercury PTWI and about 13% above the methyl-mercury PTWI. These values were compared to the values of total and methyl-mercury in hair (3). The concentration of the total mercury found in hair was 1.3–12.9 μg/g and of methyl-mercury 1.1–10.8 μg/g. It was concluded that it did not reach the critical level at which the toxic effect of mercury could be expected.

CONCLUSIONS

The daily lead and cadmium diet intake of general population in Croatia is much lower than the PTWI values proposed by WHO. Population living on the Adriatic coast and islands consumes more total and methyl-mercury through seafood than the inland population and its daily intake of mercury is closer to PTWI.

REFERENCES

1. Buzina R, Subotičanec K, Vukušić J, Sapunar J, Antonić K. Effect of industrial pollution on seafood content and dietary intake of total and methylmercury. Sci Tot Environ 1989;78:45–57.
2. Blanuša M, Telišman S, Hršak J, Fugaš M, Prpić-Majić D, Šarić M. Assessment of exposure to lead and cadmium through air and food in inhabitants of Zagreb. Arh Hig Rada Toksikol 1991;42:257–66.
3. Buzina R, Stegnar P, Buzina-Subotičanec K, Horvat M, Petrić I, Farley TMM. Dietary mercury intake and human exposure in an Adriatic population. Sci Tot Environ 1995;170:199–208.
4. Sapunar-Postružnik J, Bažulić D, Kubala H, Balint L. Estimation of dietary intake of lead and cadmium in the general population of the Republic of Croatia. Sci Tot Environ 1996;177:31–5.
5. Ivčić N, Simeon Vl, Weber OA. Olovo u pitkoj vodi u gradu Zagrebu [Lead in the drinking water in the city of Zagreb, in Croatian]. Arh Hig Rada Toksikol 1982;33:259–64.

6. Najdek M, Sapunar J. Total and methyl-mercury content in bivalves, *Mytilus galloprovincialis* Lamarck and *Ostrea edulis* Linnaeus: relationship of biochemical composition and body size. Bull Environ Contam Toxicol 1987;39:56–62.
7. Srebočan E, Srebočan V, Pompe-Gotal J. Kadmij: izvori i kontaminacija domaćih životinja (Cadmium- sources and contamination for domestic animals, in Croatian). Veterin arh 1991;61:207–15.
8. Zvonarić T. The cycling of mercury through the marine environment of Kastela Bay. In: Gabrielides GP, editor. Proceedings of the FAO/UNEP/IAEA Consultation Meeting on the Accumulation and Transformation of Chemical Contaminants by Biotic and Abiotic Processes in the Marine Environment; 24–28 Sep 1990; La Spezia, Italy. Athens: UNEP; 1991. p. 369–81.
9. Čulin S, Zvonarić T. Content of total mercury and methylmercury in some commercial fish species of the Middle Adriatic area. Prehrambeno-tehnol biotehnol rev 1995;33:133–7.
10. Bošnir J, Puntarić D. Lead concentration in brassicas from Zagreb home gardens. Croatian Med J 1997;38:143–6.
11. Bošnir J, Puntarić D, Šmit Z, Capuder Ž. Fish as an indicator of eco-system contamination with mercury. Croatian Med J 1999;40:546–9.
12. Jureša D, Blanuša M. Total contents of mercury, lead and cadmium in common edible fish and mussel from the Adriatic Sea [abstract]. In: Szteke B, Kabata-Pendias A, Jedrzejczak R, editors. Abstract Book of the 1st International IUPAC Symposium Trace Elements in Food; 9–11 Oct 2000; Warsaw, Poland. Warsaw: IUPAC; 2000. p. 66–7.
13. Global Environment Monitoring System (GEMS). Assessment of Chemical Contaminants in Food. Report on the results of the UNEP/FAO/WHO programme on health-related environmental monitoring. London: UNEP/FAO/WHO; 1988.
14. Blanuša M, Breški Đ. Contribution to resolving analytical problems of lead and cadmium determination in food and faeces. In: Farmer JG, editor. Proceedings of the International Conference »Heavy Metals in the Environment«; Edinburgh, UK. Volume 1. Edinburgh: CEP Consultants Ltd; 1991. p. 597–600.
15. Prester Lj, Jureša D, Blanuša M. Decomposition of fish samples for determination of mercury. Arh Hig Rada Toksikol 1998;49:343–8.
16. Vađić V, Jukić J. Trendovi kakvoće zraka u Zagrebu (Trends of air quality in Zagreb, in Croatian). In: Šega K, Fugaš M, Vančina F, editors. Zbornik radova Prvog hrvatskog znanstveno-stručnog skupa »Zaštita zraka '97«, Crikvenica 1997. Zagreb: Hrvatsko udruženje za zaštitu zraka; 1997. p. 161–8.
17. Hršak J, Šega K, Bešlić I, Balagović I. Lead and cadmium content in PM_{10} and $PM_{2.5}$ particle fractions in Zagreb air. In: 12^{th} Regional Central European Conference IUAPPA and 4^{th} International Conference on Environmental Impact Assessment; 11–14 Sep 2000 Prague, Czech Republic. Prague: IUAPPA; 2000. p.124–6.
18. Vahter M, Berglund M, Slorach S, Friberg L, Šarić M, Xingquan Z, Fujita M. Methods for integrated exposure monitoring of lead and cadmium. Environ Res 1991;56:78–89.
19. Goyer RA. Nutrition and metal toxicity. Am J Clin Nutr 1995;61 Suppl:646S–50S.
20. Food and Nutrition Board, Commettee on Dietary Allowances. Recommended Dietary Allowances, 9^{th} ed. Washington (DC): National Academy of Sciences; 1980.
21. Blanuša M, Jorhem L. Dietary intake of some essential elements in Sweden and Yugoslavia. In: Momčilović B., editor. Seventh International Symposium on Trace Elements in Man and Animals (TEMA-7); 20–25 May 1990; Dubrovnik, Croatia. Zagreb: IMI; 1991. p. 13/8–10.
22. World Health Organization (WHO). Trace Elements in Human Nutrition and Health. Geneva: WHO; 1996.
23. Horvat M. Študije in razvoj analiznih metod za določanje nizkih koncentracij živega srebra in njihova uporaba pri analizi bioloških vzorcev in vzorcev iz okolja ŠStudies of development of methods for determination of low concentrations of mercury and application for its determination in biological and environmental samples, in Slovenian, dissertationĆ. Ljubljana: University of Ljubljana; 1989.
24. International Programme on Chemical Safety (IPCS), Environmental Health Criteria 86, Mercury – Environmental Aspects. Geneva: WHO; 1989.

25. Horvat M, Zvonarić T, Stegnar P, Prosenc A, Konda D, Sabadin A. Relation between total mercury, methylmercury and selenium in fish muscle from the Adriatic Sea. In: Vernet J-P, editor. International Conference Heavy Metals in the Environment; Geneva, Switzerland. Vol 1. Edinburgh: CEP Consultants Ltd; 1989. p. 370–3.
26. Mikac N, Picer M. Mercury distribution in a polluted marine area. Concentrations of methyl mercury in sediments and some marine organisms. Sci Tot Environ 1985;43:27–39.
27. Vukadin I, Zvonarić T, Odžak N. Fate and distribution of toxic heavy metals in some marine organisms from the eastern Adriatic coast. Helgolännder Meeresunters 1995;49:679–88.
28. Odžak N, Zvonarić T, Kljaković Gašpić Z, Horvat M, Barić A. Biomonitoring of mercury in the Kaštela Bay using transplanted mussels. Sci Tot Environ 2000;261:61–8.

Sažetak

UNOS OLOVA, KADMIJA I ŽIVE HRANOM U HRVATSKOJ

Prikazani su podaci o unosu olova, kadmija te ukupne i metil-žive hranom u općoj populaciji Republike Hrvatske. Posebna pozornost posvećena je podacima objavljenim u posljednjih deset godina. Opisane su najčešće primjenjivane metode za kvantitativno određivanje ovih metala u biološkom materijalu. Navedeni su objavljeni i vlastiti neobjavljeni podaci o koncentracijama olova i kadmija u povrću, ribama, školjkama i organima domaćih životinja sakupljenim u neonečišćenim seoskim područjima. Također su navedene koncentracije žive u ribama i školjkama iz onečišćenih i neonečišćenih područja uz Jadransko more. Dnevni unos olova i kadmija hranom procjenjivan je različitim metodama: metodom analize elemenata u sakupljenim uzorcima dvostrukog dnevnog obroka i proračunom iz podataka o potrošnji hrane prema statističkom godišnjaku Republike Hrvatske. Dnevni unos ukupne i metil-žive određen je prehrambenom anketom o navikama uživanja morskih plodova. Zaključeno je da unos olova i kadmija hranom u općoj populaciji iznosi 6–40% od privremeno dopuštene količine tjednog unosa hranom prema Svjetskoj zdravstvenoj organizaciji (*provisional tolerable weekly intake*, PTWI). Ovisno o metodi određivanja, PTWI vrijednosti jesu 1.600 μg olova i 450 μg kadmija po osobi. Populacija koja unosi najviše ukupne i metil-žive je ona koja živi u Jadranskom priobalju i na otocima. Njihov unos hranom je blizu PTWI vrijednosti koje iznose 300 μg ukupne žive i 200 μg metil-žive po osobi.

Ključne riječi:
atomska apsorpcijska spektrometrija, dvostruki dnevni obrok, metil-živa, povrće, ribe, školjke

Requests for reprints:

M. Blanuša, Ph. D.
P. O. Box 291, HR–10001 Zagreb, Croatia
E-mail: *mblanusa@imi.hr*