EVALUATION OF ACTUAL STATUS OF SELENIUM AND MERCURY IN POLISH AGRO-SYSTEMS

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One of the main problems in estimation of mineral resources and their biologically active forms in the ecosystem is a choice of biomarkers. McCarthy and Munkittrick (1) defined biomarkers as functional measure of exposure to stressors. Free-living animals are worldwide recognized and accepted as environmental pollution bioindicators. Game animals are directly exposed to the influence of xenobiotics polluting the whole ecosystem. In long-term evaluations changes caused by stressors may concern behavior, physiology, biochemistry and/or genomic structure and function. Results of its tissue toxicological, biochemical and anatomopathological investigations provide much more detailed information and the transposition of these results to humans seems to be much more appropriate than i.e. extrapolation of laboratory studies based on the use of just few invertebrate species. Such studies may have been chosen for their uncomplicated culture and sampling rather than ecological relevance.

From essential elements selenium was chosen as a main trace element because of its crucial importance in human and animal health. The importance of heavy metals pollution of polish agro-ecosystems will be evaluated based on mercury contamination.

Selenium level in Polish agro-ecosystems

Natural selenium toxicosis is rare problem in the world and does not appear in Poland. In USA only 7 states reported naturally developing toxicosis of this trace element. However, cases of over supplementation were observed in 15 states. In 4 states toxic effects of Se in aquatic environment were reported (2). Selenium contamination of aquatic habitats is associated with a broad spectrum of human activities. Such effects of Se supplementation might be also a problem in areas recognized as Se-deficient. Se supplementation is there a common practice but this situation raised a question concerning safety of such supplementation. When Se is administered directly to animals there is no reason to believe that the very low levels of Se given to livestock would significantly affect the agro ecosystem. Ullrey (3) calculated the contribution of this dietary supplementation to be below

0,3% of environmental Se. Quit different situation may appears when this trace element is added to mineral fertilizers in amounts to 10 g/ha. Fertilizer amendment technologies may cause appearance of local poisoning especially after heavy rains leading to dramatic increase of Se in run off waters. Evidence was accumulating that use of Se-enriched soil fertilizers as well as directs dietary supplementation of humans might cause higher amount of Se consumption than is usually considered as nutritionally necessary. Concern about Se deficiency influence on human health caused that in Finland it was mandated to use Se enriched fertilizers in croplands. However, initially used Se concentration appeared to be too high. This example is showing that even in Se-deficient ecosystems there is also a need of Se status assessment not only because health but also safety reasons. However, soil enrichment using Se salts are not used in Poland and the only signals of Se poisoning were very rare and caused by mistakes during medicated diet preparations.

Many cases of Se deficiency in Poland were reported in different husbandry animal species including horses, sheep and cows (4, 5, 6). In horses Se deficiency symptoms are muscular stiffness and very often foals are unable to nurse. At necropsy alopecia and degeneration of skeletal muscles are stated. Low Se level in grass is the main factor having adverse effect on lamb production. The manifestation of white muscles disease affects mostly lambs to 10 weeks of age and the reduced growth rate is noticed. Sudden death, a prominent feature of Se deficiency, hepatic necrosis, lungs edema and bilateral muscle paleness of skeletal muscles (white muscles disease) are often found in pigs. Areas of Se deficiency have been mapped worldwide (7). Based on Se concentration analysis of cows' milk, it was calculated that on about 80 % territory of Poland moderate or severe Se deficiency appears. For Se level evaluation cows' milk was chosen because, as it was shown, it relates to Se concentration in serum and muscles, and also because of low cost and easy method of sample collection. The only problem is very low Se concentration in the skim cow milk, what might create analytical problems. It was shown that in cows, which were not subjected any form of Se supplementation, its milk concentration related to this trace element level in ecosystem and in free living animals. Among game animals hare (*Lepus* europaeus Pall.) is the accepted bioindicator of xenobiotics, heavy metals and trace elements (8). However, the population of these animals is constantly decreasing. Muskrats (*Ondatra zibethica*) are very popular in Poland and they burrow in banks of ponds and streams. In opposite to hare population of these animals increasing however, its expansion is lately slowing down because of growing appearance of wild mink. Using these two species of free-living animal high geographical variation among examined territories of Poland was stated. Despite of analyzed material, the lowest level of Se in all analyzed samples originated from Olsztyn province in northeastern Poland. Grzebula (9) observed in south-eastern part of Poland appearance of the nutritional muscular dystrophy in horses, sheep and cattle, as well as disturbances in reproduction, typical for Se deficiency. All this indications suggest that whole eastern part of Poland is Se deficient.

The highest Se concentrations were observed in samples obtained in southwestern part of Poland (Legnica province). That area known as a Copper Basin is one of the regions in the greatest ecological danger in our country. Grodzinska et al. (10) were found that Silesia Industrial Region posses in samples of moss the highest concentration of the majority of trace elements and heavy metals and only mosses originated from Legnica Copper Basin were richer in Cu and As. A very high dust emission, containing also $Se0_2$, H_2SeO_3 and elemental Se are also emitted during industrial coal combustion. This emission of Se is the main source of Se found in animal samples originated from this region. The highest Se concentration among examined tissues was found in the liver of muskrat. About 40 times lower values were found in the cow's milk. Both in the state of selenium deficiency and in cases when the Se requirement is met the existence of a correlation between Se content in the fodder and in the cow milk was observed (11). It means that in Se-deficient territories in unsuplemented cows its milk is a good indicator of Se-status not only of its own body but also the agro-system. The use of free-living animals as bioindicators of Se status does not have these kinds of restrictions. However, we cannot forget that development of selenium standard for wildlife is also necessary (12). In Se-deficiency conditions recognized in Poland the use of salt-mineral mixtures fodder enrichment or in form of licks is necessary. In material used in these free-choice methods of supplementation the recommended Se concentration is 20-30 ppm. The NRC has proposed a maximum tolerable level of Se in the diet to 2 ppm. This safe level of Se would allow a reasonable safety factor between the nutritional requirement and the maximum tolerated level allowed to use in the diet. We cannot forget however about the influence of selenium on other trace elements and heavy metals availability and their action. Potter and Mattrone (13) demonstrated protective effect of se supplementation on survival time and methyl-mercury neurotoxicity in rats. Simultaneous increase of selenium and mercury tissue accumulation in mercury miners was observed by Kasta et al. (14). Authors were suggested that elevation of tissue retention of Se together with Hg might be a natural mechanism leading to a decrease of mercury toxicity. Also Zarski et al. (15) evaluating Se and Hg level in tissue of hares obtained in different regions of Poland noticed a statistically significant positive correlation between these elements.

Mercury pollution

A widespread use of mercury in industry and agriculture caused an increase of its demand, however in Poland total emission of Hg is decreasing since 1996. The highest total emission was 33,6 tons observed in 1996 and now is below 20 tons data published in Rapport of Ecological Environment Status (Raport Stanu Srodowiska-2003) (16). An important source of mercury pollutions is coal and oil combustion. The participation of Silesia Industrial Region is 3,4 t and Opole region (where Legnica Copper Basin is located) 2,1 t. In contrast to such high Hg emission noticed in these industrial northeastern areas of Poland – Warminsko-mazurskie the local Hg emission in 2002 was only 0,18 t (16). In Poland the average concentration of Hg in soil estimated in 2003 was 0,036 mg/kg (GUS 2004). High variation of soil contamination among different regions was stated and i.e. northeastern region of Poland (typical small farming area) this concentration was 0,028 but in soil samples from Silesia region this concentration was as high as 0,333 mg Hg/kg. The results obtained by Szymczyk-Kobrzynska and Zalewski (17) show that Warminsko-mazurski region is an area characterized by low xenobiotics pollution. Authors were analyzing pollution of natural environment by chlorinated hydrocarbons and polychlorinated biphenyls using red deer obtained in years 2000/2001. Analysis of chemical composition of some plants can serve as a good indicator of natural environment pollution. The use of terrestrial mosses as bioindicators of heavy metal deposition from atmosphere is well established. Grodzinska et al. (18) published results of such monitoring study performed in Poland. They found the highest Hg concentrations in examined mosses from Silesia Industry Region. Only Cu and As concentration were higher in samples from Legnica Copper Basin. These results are in conformity with load of Hg observed in theses areas. Statkiewicz and Gayny (19) estimated Hg concentrations in mushrooms growing wild in different regions of Poland. Authors conclude that, in opposite to cadmium, mercury concentration in dried mushrooms do not cause any excitement in light of the FAO/WHO agreements. Taking into account noticed Hg concentrations in wild mushrooms obtained in north-central part of Poland, the flesh of mercury from mushrooms consumption may not pose hazards to human health even at a consumption rate of 28 g mushrooms DM/day (20). The study of Migaszewski et al. (21) estimated chemical variability derived elemental concentrations in the soil and *Pinus sylvestris* (Scots pine) needles and bark. They noticed that the chemistry of subsoil yields was even shoving greater diversity than topsoil and that maximum allowable Hg concentration for individual plant species do not seem to be hazardous to living organisms.

An important source of environmental pollution is also agriculture. Mercury compounds were used as seed mordant and grains treatment with such compounds leaded to soil pollution with this heavy metal in amount up to 10 g Hg/ha (22). As a result of several cases of man and animal poisoning noticed in Poland, the production of mercury seed dressings was discontinued in 1978, however even several years later they were still found in many farms. Many scientists agree that the honeybee (*Apis mellifera* L.) and its products can serve as summary test of environment pollution. The average concentration of Hg in the body of bees from different regions of Poland was very low (0,007 mg/kg BW) as well as its concentration in honey 0,003 mg/kg BW (23). In Poland material obtained from apiaries located near to firing ground in Drawsko was found to have much higher Hg concentration. According to norms of admissible food contamination, which is 0,01 mg/kg, the observed Hg concentrations in honey are very low.

Free-living animals are accepted as a good bioindicators of environment contamination. The toxicity of heavy metals is compounded by their persistency in the environment, accumulation in living organism and selective effect of some biological systems. Free-living animals are highly depending on local ecosystem because of their close relation to natural food sources and direct contamination caused by heavy metals concentration in dust particles in the air. Heavy metals as abiotics preferentially accumulate kidney, liver and muscles. The critical organ in case of Hg is kidney; especially the cortex. The rate of local industrialization and intensity of agriculture production have significant influence on Hg content in the tissue of hare. The concentration of Hg in the muscles of hare obtained in small farms areas (without any industry) was 0,002, commercial farm areas 0,004 and heavy industry area 0,007 mg/kg BW (24). Much higher differences were noticed in Hg concentrations in liver and kidney where in cortex the average concentration of animals from heavy industry mils and coal mines region 0,126 mg Hg/kg BW was observed, comparing to over 3 times lover level observed in hares from small farm areas. Comparison of Hg content of studded hares with domestic rabbits from analogical locations has shown much lower concentrations of mercury in tissues of rabbits. Obtained results confirmed that the concentration of Hg in the tissue of hares well reflects the rate of mercury pollution of examined area. Comparison of mercury pollution based on its concentrations in roe deer tissue obtained in different regions of Poland showed also high variation (25). It was noticed that Hg concentration in muscles of roe deer from northeastern region of Poland was 0,002 mg/kg BW comparing to 0,007 and in kidney cortex 0,007 and 0,114, respectively.

According to the Main Statistical Office (GUS - 2002) in 2000 the amounts of mercury in game animal tissues in Poland were as follow: muscles 0,004, liver 0,008 and kidneys 0,035 mg/kg BW. Only in case of kidneys maximal noticed level of Hg 0,254 mg/kg BW excide the highest permitted content (HPC) (0,05 mg/kg BW). Observed amounts for muscles were below HPC – 0,02 mg/kg BW, as well for liver – 0,05 mg/kg BW.

Much higher concentration of mercury was noticed in fish (carp) – 0,024 mg/kg BW. This result is still relatively low in comparison with concentration of Hg noticed in tissue of breams (*Abramis brama* L.) caught, in 1990, in the middle course of Vistula River – 1,065±0,214 mg/kg BW (26). The concentration noticed in bream's excide HPC (0,5 mg/kg BW). Mercury is poorly dissolvable in the water and its leads to Hg precipitation in bottom deposits where such fishes as burbots and breams use to feed. From the information's of Ministry of Agriculture published by Main Statistical Office in 2003 average mercury concentration in analyzed samples was highest lax 0,71 and lowest in sprat 0,25 mg/kg BW. These data suggest that in many cases the concentration of Hg in Baltic Sea fishes and also in fishes caught in rivers excide HPC.

All of human activities (industrialization, agriculture) caused an increase of mercury content in the food chain to the last decade of 20th century. Then the constant trend to decrease of both emission and noticed Hg pollution have been observed. Termination of Hg containing seed mordant use in agriculture caused that industrialization is a main source of Hg contamination of ecosystems. However, in agro-ecosystems besides air pollution, landfill sites and municipal dumping sites left uncontrolled are the main sources of Hg contamination. The knowledge of ecosystems contamination with heavy metals is extremely important not only because of ecosystem pollution evaluation necessity, its impact on animal production but also its influence on human health. High geographical variation in both mercury and selenium were noticed. Free-living animals seem to be excellent bioindicators not only helpful evaluation of heavy metals pollution but also in assessment of essential elements in ecosystem. There is a lack of multifactorial field studies involving scientists of many different specializations to illustrate relevance of environmental safety monitoring. There is also a need to create an integrating strategy for environmental quality assessment.

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