Bull. Environ. Contam. Toxicol. (2006) 76:671–676

DOI: 10.1007/s00128-006-0972-4

Bulletin of Environmental Contamination and Toxicology

Environmental Pollution and Health Risk Related to Metals in the Solid Fraction and Effluent from Waste Water Treatment

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Received: 17 December 2004/Accepted: 7 February 2006

Various human activities lead to chemical compounds being discharged into the environment. While some metal compounds are essential to animals and humans, other are known to be toxic and the environmental impact of many of them remains to be elucidated. Nevertheless, these contaminants together represent a threat both to the aquatic and soil ecosystem, and eventually to animal and human health.

Separation of arable land and livestock farming has upset the nutrient cycles that were typical of traditional, integrated farming systems. A consequence of this trend has been a significant increase in the quantities of animal excreta produced in some countries and the necessity to treat them in waste water treatment plants (WWTP). Re-use of the solid fraction from this treatment by application to cropland is associated with some risk with regard to micro-organisms, parasites, nutrients, but also some metals.

The progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC in all EU Member States is increasing the quantities of sewage sludge requiring disposal. The annual world-wide production of sludges from WWTP has been estimated to approx. 20 x 10^9 tonnes. The principal controversies surrounding their land application involve heavy metals and pathogens (Epstein 2002).

WWTP sludges contain far more heavy metals and other trace elements than artificial fertilisers. They may accumulate in the soil from which they can be mobilised by "triggers", such as acidification, and released to a soil solution from which they can be taken up by soil organisms and plant roots, or leached into groundwater, thus polluting the food chain or affecting drinking water quality. Some crops take up heavy metals from the soil to such levels that plants may become unfit for animal and human consumption.

The study conducted focused on determination of potential risk to animal the environment and human health associated with the re-use of solid fractions produced by WWTPs treating animal slurry and sewage and the quality of WWTP effluent, focusing on cadmium, lead, copper and zinc.

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MATERIALS AND METHODS

The investigations were carried in two WWTPs involving the influent and effluent and the solid fractions. The WWTP-1 treated excrements of 20 000 fattening pigs and waste waters from a village with less than 2000 inhabitants. WWTP-2 treated urban waste-waters from a conglomeration of approx. 100 000 inhabitants with very little proportion of industrial pre-treated waste-waters. Both treatment systems included mechanical and aerobic biological stages. The solid fraction of pig slurry (SFPS) is stored for different period of time and applied to agricultural land and the anaerobically treated sewage sludge (ATSS) is used as an additive to horticultural substrates or for recultivation and other agricultural purposes.
The level of cadmium, lead, zinc and copper in the influents and effluents of the WWTP and in SFPS and ATSS was determined monthly over a 6-month period by the methods of Kocourek (1992) using an atomic absorption spectrometer equipped with a graphite furnace and background correction (Unicam Solar 939). Samples for analysis of Pb, Zn and Cu were digested in a Milestone microwave oven (5 ml HNO_3 and 1 ml HCl per 1 g sample). The operating parameters (wavelength and band pass) were those recommended by the instrument manufacturer: 228.8 nm and 0.5 nm for Cd, 283.3 nm and 0.5 nm for Pb, 213.9 nm and 0.5 nm for Zn, and 324.8 nm and 0.5 nm for Cu, resp. The quantification and detection limits were 0.03 $\mu g.l^{-1}$ and 0.01 $\mu g.l^{-1}$ for Cd, 0.27 $\mu g.l^{-1}$ and 0.08 $\mu g.l^{-1}$ for Pb, 0.096 $mg.l^{-1}$ and 0.29 $mg.l^{-1}$ for Cu and 0.130 $mg.l^{-1}$ and 0.039 $mg.l^{-1}$ for Zn, resp. The flame condition and graphite furnace were optimised for maximum absorbance and linear response while aspirating known standards. The standards were prepared from the individual 1.000 mg/kg standards (MERCK, Germany). The recovery of the methods were 96-98% and reproducibility was better than 1%. All metal concentrations were obtained on a wet weight basis and the results for solid fraction were recalculated per dry matter (dm). The data are presented as minimum, maximum, mean (SEM) and standard deviation (SD) for influent, effluent and the sludge and a calculated WWTP removal efficiency for both WWTPs is provided.

The results were evaluated statistically with the software Microsoft Excel 7.0.

RESULTS AND DISCUSSION

The results obtained in our study are presented in Tables 1 and 2.

Metals are a unique class of toxicants. They occur and persist in nature and their toxicity may be drastically altered as they assume different chemical forms (Lu 1996). With regard to accumulation of heavy metals the plants are divided to three groups: excluders, indicators and accumulators. While the uptake of heavy metals by indicator plants is directly related to their concentration in the soil, accumulators (plants accumulating more than 1000 $\mu g.g^{-1}$dm) grow on stands with high concentration of metals and accumulate them regardless of their concentration in the soil. For example maize accumulates well Cu, Zn, Cd and Cr while its accumulation of Co and Pb is relatively low. Perennial grass accumulates

Zn, Cd and Pb but its uptake of Cu is lower (Gallo 2002). Distribution of metals among different parts of plants should also be considered.

Inputs of metals to the urban waste water system occur from three generic sources: domestic, commercial and urban runoff. Faecal matter typically contains 250 mg Zn kg^{-1}, 70 mg Cu kg^{-1}, 5 mg Ni kg^{-1}, 2 mg Cd kg^{-1} and 10 mg Pb kg^{-1} (dm). The other principal sources are body care products, pharmaceuticals, cleaning products and liquid wastes. The majority of potential toxic elements in raw sewage are partitioned during wastewater treatment into the sewage sludge or the treated effluent. Approximately 70-75% of Zn, Cu, Cd, Cr, Hg and other metals in raw sewage is removed and transferred to the sludge and concentrations of these elements in the final effluent would be expected to decrease by the same amount. The data on potentially toxic element content in the treated wastewater (effluent) are limited due to the low concentration, often below detection limits (European Communities 2001).

Investigations conducted in 14 European countries showed that concentrations of potentially toxic elements in sewage sludge vary considerably, for example mean Cd content in sludge in Poland was almost ten times higher than that in Finland (9.93 vs 1.0 mg.kg^{-1} dm, resp.) Pb was high in UK and low in Norway (221.5 vs 21.7 mg.kg^{-1} dm, resp) Cu in UK was more than double of that in the Netherlands (562 vs 190 mg.kg^{-1} ds, resp.) and Zn in Poland was more than ten times higher than that in Norway (3641 vs 340 mg.kg^{-1} ds, resp). Emissions of potentially toxic elements from WWTPs in Sweden and Norway in 1998 amounted to 137 and 150 kg per annum for Cd, 1464 and 1500 kg for Pb, 15 377 and 15 000 kg for Cu and 32 346 and 32 000 kg for Zn, respectively (EU Communities 2001).

Free-living animals are continuously exposed to environmental pollutants and may become an important indicator of metal pollution. Their exposure is affected by many factors, particularly by food (herbivores and omnivores) and its spectrum, species, age, sex, biotope, and others (Kottferová 1998).

Cadmium as a highly toxic metal ranks among the most hazardous metal pollutants. Cd has accumulated in some plants to levels that may be hazardous to humans. Its concentration in vegetable grown on cadmium polluted soil was higher, for example 47-340 fold in potatoes, 25-144 in rice, 9 fold in carrot, 205 in cabbage and 43 fold higher in lettuce compared to products grown on unpolluted soil. Winter cereals accumulate more Cd than the spring ones. Koréneková et al (2002) analysed samples from 35 cows from a metal-polluted area and observed that the levels reaching the highest permissible hygiene limits for Cd were recorded in 7 of the 35 samples of liver and in 2 of the 35 samples of muscle.

The concentration of lead in biological tissues corresponds to the environmental pollution and varies significantly with geographical area and demographic factors. It has no known essential role in an organism and its accumulation in tissues may cause several health hazards including neurotoxicity, hematotoxicity and reproductive disturbances (Rodmilans et al. 1996). Skalická et al. (2002)

Table 1. Partitioning of selected heavy metals in system one.

Metal	Influent ($mg.l^{-1}$)		Effluent ($mg.l^{-1}$)		Removal Efficiency (%)	Solid fraction ($mg.kg^{-1}$ dm)	
	Min - max	Mean ± SD	Min - max	mean ± SD		Min - max	mean ± SD
Cadmium	0.01-0.80	0.29±0.31	0.006-0.01	0.008±0.002	97.3	0.6-15.2	7.45±5.90
Lead	0.02-1.70	0.66±0.71	0.02-0.23	0.125±0.082	80.3	3.8-45.2	35.38±15.68
Copper	0.50-2.10	1.22±0.64	0.03-0.10	0.067±0.035	94.5	37.5-45.2	41.40±2.42
Zinc	0.32-14.5	7.15±5.86	0.12-0.44	0.27±0.12	96.2	201.2-310.2	252.40±34.96

Table 2. Heavy metals in system two.

Metal	Influent ($mg.l^{-1}$)		Effluent ($mg.l^{-1}$)		Removal Efficiency (%)	Solid fraction ($mg.kg^{-1}$ dm)	
	Min - max	Mean ± SD	Min - max	Mean ± SD		Min - max	Mean ± SD
Cadmium	0.002-0.009	0.006±0.002	<0.001		83.3	2.60-12.4	8.00±3.74
Lead	0.12-0.19	0.16±0.03	0.001-0.005	0.003±0.001	98.1	62.4-195.5	151.65±41.99
Copper	1.02-1.08	0.72±0.50	0.038-0.046	0.043±0.003	94.0	172.5-299.2	258.97±45.95
Zinc	0.80-1.91	1.23±0.43	0.012-0.018	0.014±0.002	98.9	1110.4-790.3	1464.93±248.32

found that out of 105 analysed samples, taken in the period 1995-1999 from cattle grazing on pasture polluted with heavy metals, 40 contained levels of lead reaching the highest permissible limit.

Copper is an essential trace element that is widely distributed in animal and plant tissues. The general population may be exposed to increased levels of copper in drinking water. The largest anthropogenic releases of Cu to the environment result from mining operations, agriculture, solid waste, and sludges from WWTP. Maize takes up selectively Cu, Zn, Cd and Cr (Gallo 2002). Uptake of Cu by grass is lower. Although Cu nowadays poses few problems, Cu intoxication has been recorded in intensively fed sheep and sheep grazing in metal polluted areas. Accumulation in the liver, jaundice and haemoglobinuria are characteristic signs of toxicity (Cole et al. 1993). Liming of sludge to pH of 12 increases mobility of Cu and Ni and therefore also leaching of these metals (Scancar et al. 2001). A recent prospective population study in Finland, an area with high level of Cu in drinking water, established a positive correlation between serum Cu levels and risk of acute myocardial infarction (Salonen et al. 1991).

Zinc is a cofactor in scores of metalloenzymes and is therefore an essential element but may be toxic at high levels of exposure. WHO recommended a PMTDI (provisional maximum tolerable daily intake) of 60 $mg.d^{-1}$. When in excess, it reacts with red cells and hepatocytes. Clinical signs include elevated liver enzymes (LOH, AST, SDH) and bilirubin (Murphy 1996). The study by Kottferová et al. (2002) showed that the liver is the main organ of accumulation of zinc, followed by heart, kidney and leg muscles.

Our results showed that a relatively high removal (80.3-98.9%) of the observed inorganic micropollutants was reached in both WWTP. Higher concentration of metals was present in the influent to WWTP-1 which was reflected also in the quality of the effluent. The effluent from WWTP-2 complied with the acceptable limits for Cd, Pb and Zn in surface water only the levels of Cu were approximately double. The effluent from WWTP-1 exceeded these limits but complied with the values acceptable for water for irrigation with respect to Cu and Zn but the levels of Pb (50 $\mu g.l^{-1}$) and Cd (5$\mu g.l^{-1}$) were exceeded in 5 out of 6 samplings. However, with regard to considerable dilution of the effluent in the recipient any serious problems should not be expected.

National regulations in the Slovak Republic about application of sewage sludges to the soil limit the concentration of Cd to 10 $mg.kg^{-1}$ dm, Pb to 750 $mg.kg^{-1}$, Cu to 1000 $mg.kg^{-1}$ and Zn to 2 500 $mg.kg^{-1}$ dm. The levels of investigated metals in both sludges were below these limits except for cadmium which was the main element of concern and exceeded the limit in three samples of sludge from WWTP-1 (12.5, 15.2, 11.8 $mg.kg^{-1}$) and two from WWTP-2 (10.4, 12.4 $mg.kg^{-1}$).

With regard to further dilution, the concentration of investigated metals in the effluent from sewage WWTP presents no significant risk to the surface and ground water. Higher levels of Cd and Pb and potentially also of Cu and Zn (toxicity to water fauna) from pig slurry treatment may be a subject of concern in periods with low flow rates in the recipient.

The biggest risk associated with application of sewage sludge to agricultural soil involves cadmium which exceeded the acceptable limits in almost 50% of the investigated samples. This risk may be increased when applying sludges to soil in industrially polluted areas where they may affect plants and animals and therefore the entire food chain.

Acknowledgements. The study was supported by Grant VEGA 1/0620/03.

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