

REMOVAL OF HEAVY METALS FROM PIG SLURRY BY ACTIVATED SLUDGE TREATMENT

Milada Vargová, J. Venglovský, Nada Sasáková, Olga Ondrašovičová, M.
Ondrašovič, P. Sviatko, Marija Vučemilo, Alenka Tofant

Summary

The presence and levels of heavy metals in pig excrements are a subject of concern as they may pass to those products of the treatment which are either discharged into the recipient (effluent) or are applied to the soil (solid fraction) and may pollute the environment. Through contamination of surface water and soil the metals can penetrate in the food chain of animals and humans. The aim of our study was to investigate the levels of some metals of interest in different stages of treatment of pig slurry by activated sludge (influent, effluent and solid fraction) in relation to their release to the environment and its possible contamination.

Our results showed that the effectiveness of removal of metals by the activated sludge system was high. Although the limits for presence of some metals (Pb, Hg, Cu, Zn) in surface water were exceeded in some samples of the effluent, with regard to its further considerable dilution in the recipient no serious risk to surface water quality is envisaged. The levels of dangerous heavy metals (Cd, Pb, Hg) in the separated solid fraction were far below the limits required for composted biosolids intended for application to agricultural land.

Key words: slurry treatment, heavy metals, influent, effluent, pig slurry solids

Introduction

Most hazardous substances in the environment are those, which combine persistence with biological availability. One group of such substances are

Milada Vargová, Olga Ondrašovičová, M. Ondrašovič, University of Veterinary Medicine, Komenského 73, 041 81 Košice; J. Venglovský, Nada Sasáková, Research Institute of Veterinary Medicine, Hlinkova 1/A, Košice; P. Sviatko, Institute of animal physiology, Pri Hati 1, 040 01 Košice, The Slovak Republic; Marija Vučemilo, Alenka Tofant, Department of Animal Hygiene, Environment and Ethology, Faculty of Veterinary Medicine of Zagreb, Croatia.

metals and their organic compounds, especially heavy metals. Many trace metals are natural constituents of the environment. Some of them are even necessary for the biological functions of organisms (e.g. cobalt, copper, manganese, molybdenum and zinc). At high concentration levels, however, all metals will have negative impacts, as they are easily accumulated in the food chain. Metals are emitted to the environment from many different sources, the most important ones being industries (mainly non-ferrous, power plants, iron and steel waste and chemical industries), agriculture (irrigation with polluted water, use of mineral fertilizers, especially phosphates, contaminated manure, sewage sludge and pesticides containing heavy metals), waste incineration, combustion of fossil fuels and road traffic.

Heavy metals from different sources accumulate in the soil where they are fixed on mineral particles. From there they can be mobilized by "triggers", such as acidification, and released to soil solution from which they can be taken up by soil organisms and plant roots, or leached to groundwater, thus polluting the food chain or affecting drinking water quality (Chirás, D. D., 1991, Kiliham, K., 1994). With regard to contamination of soil with heavy metals cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), mercury (Hg) and arsenic (As) represent a problem of concern (Stannerson and Bordaú, 1995).

The aim of our study was to investigate the levels of some metals of interest in different stages of treatment of pig slurry by activated sludge in relation to their release to the environment and its possible contamination.

Materials and methods

We investigated the removal of heavy metals from pig slurry during the treatment with activated sludge. The water treatment plant (WTP) investigated operates on an intensive pig fattening farm and is designed for the treatment of 823 m³/d of pig slurry. Before the treatment all excrements from pig farm (capacity for 20 000 pigs) accumulate in a collection pit. The first stage of treatment consists of mechanical separation of the solid fraction (SF) of pig slurry on vibrating sieves which amounts to about 2.8% of the total volume of raw slurry. The liquid portion obtained in this stage is pumped to a sedimentation tank and after sedimentation of additional particles is treated chemically by addition of Ca(OH)₂ to pH 11±0.5. After the chemical treatment, the liquid is pumped to the biological stage with denitrification and nitrification compartments where it is treated with activated sludge. The treated water (94% of the original volume) is discharged into the recipient (river). The remaining portion are sludges (3.2%) that are treated within the WTP process.

Determination of metals was carried out by the common AAS method in the solid fraction of slurry, influent to the WTP, and the effluent which is discharged to the surface water. Altogether 5 point samples were taken over the period of 2.5 years (January 1996 – June 1998). The content of dry matter (DM) was determined by drying aliquots of samples at 105 °C so the results can be recalculated per kg DM if necessary. As the detention time in WTP is approx. 24 h, the samples of influent, effluent and the solid fraction do not correlate.

Results and discussion

Air-breathing animals get the majority of the environmental toxicants from feed and water but not all of them will be absorbed in the intestine and may leave the body in faeces.

Treatment of such faeces in wastewater treatment plants may be associated with many problems and risk to the environment. Metals and other toxic chemicals are transferred to the solid fraction or wastewater sludge and the application of this fraction to agricultural soil may result in the uptake and accumulation of toxicants by crops and grazing animals, eventually posing a threat to humans (K o t t f e r o v á and K o r é n e k o v á, 1995, 1998). They may also adversely affect biological treatment processes which may result in reduced BOD and COD removal and reduced efficiency in separation of solids. Chemical toxicants can also diminish the quality of receiving waters and threaten aquatic organisms. Metals present in water pass to sediments, where by means of microorganisms their organic derivatives are formed and pass to the food chain of fish and eventually of man.

The activated sludge treatment provides very good removal for toxic metals such as Cd, Cr, Cu, Zn, Ni, and Pb. Metals are generally concentrated in sludges due to their sorption to flocs. Their removal depends on pH, solubility and concentration of metals, organic matter, and solid retention time. The affinity of biological solids for heavy metals was found to follow the order $Pb > Cd > Hg > Cr^{3+} > Cr^{6+} > Zn > Ni$ (B i t t o n, 1995).

The presence and levels of heavy metals in pig excrements are important as they may pass to those products of the treatment which are either discharged into surface water (effluent) or are applied to the soil (solid fraction). Our investigations focused on concentration of some metals (Cd, Hg, Pb, Cu, Zn, Fe, Ca, Mg, Mn) in pig slurry fed to the treatment system with activated sludge, in treated effluent, and the separated solids. The results obtained are presented in Table 1.

Table 1. - THE LEVELS OF METALS DETERMINED IN DIFFERENT STAGES OF THE WTP AT A PIG FARM

Parameter	Influent mg/l	Effluent mg/l	Solid fraction mg/kg
Iron (Fe)	14.4 – 33.1	0.7 – 2.3	178 – 2286
Manganese (Mn)	2.1 – 4.9	0.02 – 0.15	7.9 – 229
Calcium (Ca)	178 – 351	71 – 161	2610 – 15 405
Magnesium (Mg)	96 – 189	69 – 91	570 – 2690
Mercury (Hg)	0 – 0.011	0 – 0.005	0.003 – 0.025
Cadmium (Cd)	0.012 – 0.8	0.006 – 0.01	0.137 – 1.74
Lead (Pb)	0.02 – 1.7	0.02 – 0.23	0.533 – 5.813
Copper (Cu)	0.5 – 2.0	0.025 – 0.104	5.81 – 39.64
Zinc (Zn)	0.32 – 14.5	0.12 – 0.44	36.5 – 197.6
Dry matter (%)	0.85 – 1.34	0.06 – 0.26	13.9 – 18.39

The concentrations determined indicate a good removal of toxic metals by the activated sludge process. The content of heavy metals in the effluent was lower in the majority of samples than the concentrations of metals allowed in surface waters. However, it should be remembered that the aquatic biota are usually affected by concentrations lower than those allowed in drinking water.

The values presented also show considerable variations in the level of most of determined elements. The presence of higher levels of some metals can be explained by their supply in feed and mineral feed additives which differs considerably for different categories of pigs and may be related also to feed suppliers. As the age and composition of stock changes, the amount of these elements in the excrements will change, too. Moreover, some variations may be ascribed to the retention of excrements in the collection pit and their different affinity to solids and to the way of mixing and pumping the raw slurry before the treatment.

In association with the effect on aquatic life, the possibility of releasing from sediments or leaching from the soil especially some of the heavy metals should be monitored.

Copper and zinc may be rather poisonous to aquatic biota. Their effect depend also on water hardness. Fish and invertebrates have been reported to be affected by Cu levels as low as 10-20 $\mu\text{g Cu/l}$ in water with a hardness of 100 $\text{mg CaCO}_3/\text{l}$ so it is recommended to keep Cu levels below 40 $\mu\text{g Cu/l}$. With regard to zinc the recommended water standards for fish are below 300 $\mu\text{g Zn/l}$ in water with a hardness of 100 $\text{mg CaCO}_3/\text{l}$ but below 30 $\mu\text{g Zn/l}$ in water with a hardness of 10 $\text{mg CaCO}_3/\text{l}$ (Stanners and Borda, 1995).

Cadmium ranks among the most hazardous metal pollutants. The cadmium that is discharged into inland surface waters accumulates in the sediment. It has a very high accumulation coefficient. Its levels in surface waters should not exceed 10 µg/l. The accepted daily human intake level of cadmium recommended by WHO is as low as 64 µg.

Considerable portion of lead is removed by sorption on base sediments. Although lead is easily transported over long distances through the atmosphere, it seems to have high tendency to concentrate in the vicinity of the point discharge. Its concentration in surface water should not exceed 50 µg/l.

Mercury is a heavy metal poison whose influence is cumulative and whose effects on neurological behaviour are notorious. Because of this an intense effort is under way to trace the sources of all mercury pollution in order to eliminate them. However, the toxicity of Hg very much depends on the physical and chemical states of the element. Biological processes in river sediments can transform mercury into the more toxic and mobile forms, mono- and dimethyl mercury. These forms are more fat-soluble and have a higher tendency to penetrate e.g. the blood/brain barrier and the placental barrier of animals. In addition, methyl mercury is persistent as it has a biological half-life of approximately two years, and will thus accumulate in the food chain. (Backlund, P., et al., 1993). The maximum acceptable limit of Hg for surface water is 0.5 µg/l.

Our results showed that the limit for Cd was not exceeded in the effluent while Pb and Hg were exceeded in 3 out of 5 examined samples. Cu level was also higher in 3 out of 5 and Zn in one out of 5 samples. The increased levels of Pb and Hg coincided in two samplings. However, the effluent is diluted considerably after it enters the recipient so serious problems should not be expected because of its quality. Examination of sediments downstream from the point of discharge could provide some additional valuable information.

The separated solid fraction of pig slurry is used most frequently for application to soil. However, with regard to its potential microbiological and parasitological contamination, it should be treated biothermically before application to cropland (P a ě a j o v á et al., 2000).. As the water content of the separated solids is too high for aerobic processes, some bulking materials should be added to achieve optimum conditions. The levels of heavy metals in the compost obtained should not reach thresholds which can damage either soil fertility or the food chain (Tab.2).

The determination of metals that raise the main concern with regard to their accumulation in soil, uptake by plants and penetration to food chain in the solid fraction from the examined WTP showed that their levels were far below the limits presented in Table II. Therefore no serious accumulation of

cadmium, lead, mercury or some other metals may be expected after manuring of crops with this substrate. However, when some bulking materials are used for composting of this fraction, care should be taken that they are of good quality also with regard to the content of heavy metals.

Tab. 2. - EXAMPLES OF POLLUTANT LIMITS FOR BIOSOLIDS APPLIED TO LAND

Pollutant	USEPA (1994B) – USA			STN 46 5735 – Industrial Composts – SR	
	CCL mg/kg	PCL mg/kg	CPLRL kg/ha	Class I mg/kg DM	Class II mg/kg DM
Arsenic	75	41	41	10*	20*
Cadmium	85	39	39	2	4
Chromium	3000**	1200**	3000**	100	300
Copper	4300	1500	1500	100	400
Lead	840	300	300	100	300
Mercury	57	17	17	1.0	1.5
Molybdenum	75	-	-	5*	20*
Nickel	420	420	420	50*	70*
Selenium***	10	36	100	ND	ND
Zinc	7500	2800	2800	300	600

CCL – ceiling concentration limits; PCL – pollutant concentration limits; CPLRL - cumulative pollutant loading rate limits

Class I, Class II – frequency of application of the two classes differs according to contamination and pH of soil. Class II cannot be used for manuring of crops intended for direct consumption

*Determined when higher contamination may be expected

** May be deleted from the rule based on court remand consideration

***Selenium limits may be changed pending court remand reconsideration

REFERENCES

1. Backlund, P., B. Holmbom, E. Leppäkoski (1993): Industrial Emissions and toxic pollutants. The Baltic Sea Environment, Session 5, Ed. L. Rydén, Uppsala University, Uppsala, Sweden, 36 p.
2. Bitton, G. (1994): Wastewater microbiology, Wiley/Liss, Inc., New York, 478 p.
3. Chiras, D. D. (1991): Environmental Science, the Benjamin/Cummings Publ. Co, Inc., California, USA, 549 p.
4. Killham, K. (1994): Soil ecology, Cambridge University Press, 242 p.
5. Kottferová, J., B. Koréneková (1995): The effect of emissions on heavy metals concentrations in cattle from the area of an industrial plant in Slovakia. Arch. Environ. Contam. Toxicol., 29, 400-405.

6. Kottferová, J., B. Koréneková (1998): Bull. Environ. Contam. Toxicol., 60, 171-176.
7. Pačajová, Z., J. Venglovský, N. Sasáková, I. Plachá (2000): Viability of selected groups of microorganisms in the solid fraction of pig slurry amended with zeolite. Xth Int. Con. on Animal Hygiene, Maastricht, the Netherlands, 1051- 1055.
8. Stanners, D., P. Bourdeau (1995): Europe's Environment, The Dobříš Assessment. EEA, Copenhagen, 712 p.

UKLANJANJE TEŠKIH METALA IZ TEKUĆEG GNOJA SVINJA OBRADOM S AKTIVNIM MULJEM

Sažetak

U radu je istraživana prisutnost i koncentracija teških metala u svinjskom gnoju koji nakon obrade mogu dospjeti u vodotoke – tekuća frakcija, ili u tlo (kruta frakcija) te tako mogu zagaditi okoliš.

Kontaminiranom površinskom vodom i tlo metalni mogu dospjeti u hranidbeni lanac životinja i ljudi.

Cilj ovog rada bio je istražiti razinu nekih metala u svinjskom gnoju nakon obrade s aktivnim muljem. U različitim fazama obrade (utok gnoja, tekuća i kruta frakcija) određene su koncentracije metala i mogući učinak na kontaminaciju okoliša.

Rezultati pokazuju veliku učinkovitost uklanjanja metala sistemom obrade aktivnim muljem. Iako su u nekim uzorcima tekuće frakcije koncentracije metala (Pb, Hg, Cu, Zn) veće od dozvoljenih graničnih vrijednosti za površinske vode, može se uzeti u obzir i daljnje razrjeđenje u prijemniku, tako da ne postoji ozbiljan rizik za površinske vode. Razine teških metala (Cd, Pb, Hg) u separiranoj krutoj frakciji gnoja su daleko ispod dozvoljenih graničnih vrijednosti za kompostirane biotvari koje su namijenjene nanošenju na poljoprivredne površine.

Ključne riječi: obrada tekućeg gnoja, teški metali, utok gnoja, tekuća frakcija, kruta frakcija

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