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HEAVY METALS ACCUMULATION IN WASTEWATERS SLUDGES

State of the knowledge on the hazards involved with land disposal of municipal sludges is presented. Sources of origin of heavy metals, both man-made and natural, are depicted. Average metal contents of sludges from different municipalities is presented and discussed. In conclusion, present assumptions as to the sources of mercury, cadmium, lead and nickel, i. e. metals considered toxic in the food chains are given. This is followed by delineation of sources of metals that the authors do not consider toxic in food products i. e. zinc, iron, copper and chromium.

1. INTRODUCTION

Land application of sewage sludge is not a new practice. It has been used by man for thousands of years, both as a means of disposing of organic wastes produced by society and as a method of soil enrichment to increase productivity. In recent years, several popular and technical articles have advocated a return to this practice. They point out that sewage sludge should not be considered as a waste product to be disposed of, but rather a valuable resource which could be recycled and even marketed because of its fertilizer value. The concern is intensified because with the continually larger percentage of the population served by sewage treatment, and the regulatory requirement for best practical control technology (BPT), the volume of sanitary solids requiring ultimate disposal is rapidly expanding. The alternative means of disposal are rapidly disappearing because they are neither cost effective, nor are they meeting our environmental and best land usage goals.

When considering the use of the accumulating organic solids for soil reclamation and land fertilization, we have to take into consideration the fact that the sludges are contaminated to a variable extent with heavy metals [1–9]. Some of these metals are extremely toxic to mammals and since plant life is capable of resolubilizing them, they can be incorporated into the food chain; others are known to accumulate in the soil and can become inhibitory to plant growth [10–15].

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Our aim at this time should be to recognize these facts, become aware of the level of contamination that can be expected in each area treatment plant, and attempt, through an educational and subsequently regulatory effort, to create a safe environment, not only with our wastewater treatment practices, but also aim for the protection of the land and the atmosphere.

2. HEAVY METALS AND THEIR CONCENTRATION IN SEWAGE SLUDGE

The term "heavy metals" refers to a number of elements including iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cobalt (Co), molybdenum (Mo), selenium (Se), chromium (Cr), nickel (Ni), boron (B), cadmium (Cd), mercury (Hg), arsenic (As), and lead (Pb). Depending on local industries, other heavy metals may be a problem in a particular locality. Contamination with some unusual metal, such as, for example, molybdenum, vanadium, or selenium, could be due to industrial activity such as metal working, smelting, mining, ore trucking, or an unusual enrichment of the local soil and thereby accumulation from street runoff [16]. Such metals as iron, zinc, copper, nickel, chromium, and lead are always present in significant concentration [17].

Weathering of the rocks, volcanic activity, silt deposits from floods, atmospheric wash-out of dust, etc., have provided from time immemorial a certain trace metal distribution on land. Some estabilished low-level metal content is necessary for plant growth. In some areas, the fertilizer has to be enriched by the particular metal needed for the crop desired to be raised. Our concern is not due to the fact that these metals are present whenever we analyze a sewage sample, but rather because the concentration we find in some areas or in some samples exceeds the anticipated level [18]. Sufficient research data has been accumulated, indicating that the uptake and accumulation of metals in the plants can be acknowledged as a hazard. Our concern is not necessarily limited to agricultural crops alone. Vegetables grown in the garden can be even more harmful because one family or a group of families' intake of food is tainted. Neither can we say that using the sludges for soil builders, as an example on stripped land, is free of these same hazards. Toxis effects on grazing and browsing animals should be as much our concern as self preservation. Neither can we say that the land we try to reclaim should be useless for future generations. The regulatory maxima stipulated by some of the other countries (England, Sweden, Holland) for each of the metals can be considered as a useful guide until our own regulatory machinery has caught up with the issues.

While we have been sampling the natural watercourses, drinking water supplies, and wells, very meagre effort was expended into monitoring the metal content of the sanitary solids. The available information itself is not easily assimilated. The sludges do not lend themselves for a simple sampling technique. There is no assurance that the analysis is representative of the existing conditions. Sampling is not frequent and the reports do not explain either the method of sampling or the frequency. Some results are quoted from raw waste, some from digested sludge, some on wet, some on dry basis. Very few reports contain analytical results on cadmium, for instance. We should at least screen the sludges periodically for all the metals, to ensure that some local conditions or industrial discharges which could render the sludges harmful to the population or agriculture, will not remain undetected. We would like to recommend the establishment of uniform practices for sampling, analysis, qualitative screening tests and reporting.

Basically the problem is caused because the relatively minor metal contamination of the influent into the sewage treatment plant is retained and accumulated with the organic solids. A high percentage of the soluble metal content is precipitated or adsorbed on sewage solids [19]. Nearly all the insoluble metals carried by the sanitary influent in suspended solid form (included also are storm waters where combined sewers are used) are retained [20, 21]. In the treatment process, the organic content is subjected to biological degradation and the total waste load ultimately discharged as solid waste is greatly reduced. No degradation or reduction will occur in the accumulated metal content; the ratio of metals to the organic content has been significantly increased. Lancy in a recent study suggests an "Accumulation Factor" of 10.000. This implies that 0.1 mg/dm^3 metal in the sanitary influent and retained as precipitated solid will ultimately amount to 1.000 mg/kg metal in the dry solids [22].

The fact that nearly the same quantity of metal carried into the rivers, lakes, dammed reservoirs, oceans, etc., as suspended solids, is buried into the silt causing no noticeable harm, does not help [23–26]. Treatment of the storm water is necessary because the magnitude of organic waste pollution caused by the non-point discharges, such as street run-off, is also desirable. Additionally, we have to concern ourselves with a continued increase of industrial pollution, metal waste due to corrosion from the homes, automobiles in the streets, etc.

A recent paper regarding analytical results from municipal sludges accumulating in 35 cities [17] illustrates very well the magnitude and variability of this pollution problem. From this, and from earlier reports by Curry, it is evident that not only heavy metals, but also PCB, Dieldrin, and other noteasily-degraded toxicants, could be accumulating to dangerous levels. The cited survey has also included analytical results from Cayuga Heights, a residential community, and from cow manure to show the comparable metal content of such generally accepted fertilizers. Table 1 is an abbreviated excerpt from the study by Furr [17].

3. PROBABLE ORIGIN OF THE HEAVY METAL CONTAMINANTS

Regulatory attention in the past was based on the assumption that nearly all the metal contaminants originate from industrial activity, especially from the metal finishing plants. No doubt these sources are significant contributors in some industrialized areas, but, in general and specifically for some metals, the total environmental load over the land or in the organic solids from sewage treatment will be hardly changed even when the stringent regulatory requirements will be met generally by the industry. Studies relating to the

Table 1

Concentration of selected metals found in municipal sludges [17]
Parts per million (dry weight)

Constituent	Atlanta	Cayuga Hgts.	Chicago	Denver	Houston	Ithaca	Los Angeles	Miami	Milwaukee	New York	Philadelphia	San Francisco	Schenectady	Seattle	Syracuse	Washington, D. C.	Cow Manure
As	3.6	3.0	29	14	20.4	4.8	26.0	10.0	3.3	8.0	16.2	6.4	21.9	30.0	26.0	6.6	4.0
Au	0.90	1.00	0.77	0.25	1.04	0.50	0.99	5.65	0.21	1.46	0.48	7.00	2.00	1.10	0.34	0.76	0.0002
Cd	104.2	6.8	14.8	46.1	111.8	66.7	171.4	149.6	443.7	29.7	192.4	8.5	22.4	64.0	200.0	31.0	0.8
Cr	1320	169	207	936	3480	650	4925	1430	14000	646	2320	1500	458	1320	1000	1260	56
Cu	1463	821	578	1370	1560	1300	2890	1200	1288	1890	2680	900	900	1170	1060	458	62
Hg	6.9	10.8	6.1	3.6	3.8	13.6	7.1	15.5	3.4	15.0	4.7	18.0	9.1	8.2	6.4	5.8	0.2
Mo	6.0	1.2	10.8	18.1	9.8	21	40	37	32.9	5.0	8.1	2.2	25.5	2.3	4.5	3.6	13.9
Ni	169	36.4	51.2	562	102	166	402	453	360	140	432	223	72	153	211		29
Pb	1445	136	605	1011	2236	329	3065	1467	2253	1976	7627	2521	598	2411	1412	498	16.2
Se	1.7	1.7	1.7	3.5		4.6	8.7	2.9	1.7	2.7	3.4	3.0	4.7	2.7	2.1	1.9	2.4
Sn	146	128	166	161	234	111	209	289	133	202	492	133	189	373	191	291	3.8
Zn	2838	560	1160	2860	2560	1700	4590	1400	1370	1340	6890	601	1090	1830	1840	1475	71

metal content in the sanitary effluent from residential areas, urban storm run-off, contaminants encountered in snow removal, etc., are most enlightening [29–34].

Because the alternative means for the ultimate disposal of sanitary solids are even more hazardous for the environment (ocean dumping, incineration), many municipal treatment plants dispose of their sludge as fertilizer. Some of the treatment plants allow truck haulage of their waste directly for land application. In some areas the wet sludge is pumped directly to the land and some even package dried sludge as salable or free supply of ready fertilizer. Since we recognize that these hazards exist, it is imperative that we become aware of the sources of these contaminants, to be able to reduce the contaminant load. It will be necessary to change our approach and instead of concentrating our efforts on an all-out attack to reduce water-borne pollution, caused by industrial or residential sources, we should become aware of the pollutional load caused by dust and the stationary and moving sources of atmospheric contaminants [35–46].

In the following we are trying to provide a brief summary of our present assumptions regarding the various probable sources (in the order of their probable magnitude) of heavy metals most generally encountered in municipal sludge.

Metals toxic in the food chain:

Mercury (mainly atmospheric) (a) atmospheric fall-out from coal burning; (b) industrial from secondary smelters, metals refining; precious metal separation, mining; (c) chlor-alkali chemical plants.

Cadmium (mainly atmospheric): (a) dust from automobile tires due to the use of impure zinc oxide in manufacturing; (b) secondary smelters, metals refining, brazing; (c) coal contaminant; (d) incineration of waste; (e) battery manufacturing and battery waste: (f) metal finishing plants (water borne).

Lead (mainly atmospheric): (a) moving sources, antiknock additive; (b) incineration of waste; smelters, secondary smelters, metals refining, galvanizing; (c) battery and secondary battery manufacturing; (d) coal contaminant; (e) metal manufacturing, metal working, soldering; (f) metal finishing corrosion products, roofs, galvanized pipe (water borne).

Nickel (mainly water borne some atmospheric): (a) metal finishings (b) corrosion products; (c) cleaning of metals in restaurants, food processing, chemical plants; (d) incineration of solid waste, coal contaminant (atmospheric).

Metals not considered toxic in food products:

Zink (atmospheric and water borne) (a) dust from automobile tires; (b) coal burning, incineration of waste, smelters, secondary smelters, galvanizers, soldering; (c) metal finishing (water borne) (d) corrosion products (water borne dust), galvanized water lines (water borne); (e) water treatment cooling, water treatment (water borne).

Copper (mainly water borne): (a) water piping, hot water heaters; (b) corrosion products, air conditioning condensers, cooling water, roofing etc.; (c) copper salt addition to water supply for algae control; (d) metal finishing.

Chromium (mainly water borne): (a) colling water inhibitor blowdown; (b) corrosion products; (c) metal finishing.

Reducing the magnitude of metal pollution can be reasonably easily accomplished when these sources are recognized and pinpointed. A better grade zinc oxide, containing a far lower level of cadmium can be stipulated for tire manufacturing, paints, pigments, ink, etc. Small secondary smelter operations can be identified and the most rigorous atmospheric control measures required. The EPA-OSHA requirements for the protection of the employees are enforced but apply only to the plant interior. Metal finishing facilities are regulated when the discharge is direct to natural waters, but yet very little control is exercised when they are located in metropolitan areas.

It is not necessary to achieve the low metal contaminant levels as found in cow manure. For example, the contaminants found in Cayuga Heights are considerably below the recommended maxima stipulated in England or Sweden. On the other hand, the cadmium levels found in Milwaukee and the lead concentration in Philadelphia are frightening, the more so because in both cities the solid waste is packaged for use as garden fertilizer.

AKUMULACJA METALI CIĘŻKICH W OSADACH ŚCIEKÓW MIEJSKICH

Praca stanowi przegląd stanu wiedzy w dziedzinie akumulacji metali ciężkich w osadach ściekowych wykorzystywanych w rolnictwie. W zarysie przedstawiono źródła pochodzenia metali ciężkich (Fe, Mn, Cu, Zn, Co, Mb, Se, Cr, Ni, B, Cd, Hg, As, Pb) z zanieczyszczeń przemysłowych powstających w przemyśle metalurgicznym, galwanizerskim i w transporcie oraz pochodzących z zanieczyszczeń naturalnych. Przedstawiono przeciętną zawartość mikroelementów w osadach ściekowych z miast amerykańskich i w osadach pochodzenia zwierzęcego. W podsumowaniu przedstawiono aktualne domniemania co do pochodzenia w osadach ściekowych metali uznanych za szczególnie niebezpieczne i toksyczne w łańcuchu pokarmowym: rtęci, kadmu, ołowiu i niklu oraz dla metali uznanych przez autorów za nietoksyczne w produktach spożywczych, w szczególności cynku, miedzi i chromu.

ÜBER AKKUMULIERUNG VON SCHWERMETALLEN IN ABWASSERSCHLÄMMEN

Der Bericht gibt einen allgemeinen Überblick über die Akkumulierung von Schwermetallen in landwirtschaftlich genutzten Abwasserschlämmen. In Grundrissen wird die Herkunft der Schwermetalle (Fe, Mn, Zn, Co, Mo, Se, Cr, Ni, B, Cd, Hg, As und Pb) besprochen. Diese entstehen vornehmlich in den metallurgischen und galvanischen Betrieben sowie im Transportwesen; sie können aber auch einen naturellen Ursprung haben.

Mittlere Konzentrationen von Spurenelementen in Schlämmen amerikanischer Kläranlagen und in Schlämmen tierischer Herkunft werden angeführt. Abschließend werden verschiedene Verursacher, die äusserst gefährliche und den ökologischen Kreislauf stark störende Metalle wie Hg, Cd, Pb und Ni in die Umwelt abgeben, aufgezählt. Nach Auffassung der Verfasser, wirken Zn, Cu und Cr in Lebensmitteln nicht toxisch.

НАКОПЛЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ В ОСАДКАХ ГОРОДСКИХ СТОЧНЫХ ВОД

В работе дан обзор состояния знаний по проблеме накопления тяжелых металлов в водосточных осадках, используемых в земледелии. Представлены источники испускания тяжелых металлов (Fe, M, Cu, Z, Co, Mb, Se, Cr, Ni, B, Cd, Hg, As, Pb) в совокупности загрязнений, образующихся в металлургической и гальванической промышленности, а также в транспорте, или являющихся результатом природных загрязнений. Представлено среднее содержание микроэлементов в водосточных осадках из американских городов и в осадках, происходящих от живытных. Обсуждается, сверх того, вопрос проникновения в водосточные осадки тех металлов, которые считаются особенно опасными и токсичными в пищейвой цепи, а именно ртути, кадмия, свинца и никеля, а также металлов, которые признаны авторами нетоксическими в продовольственных продуктах, особенно цинка, меди и хрома.

REFERENCES

[1] TARVIN D., *Metal plating wastes and sewage treatment*, Sewage and Industr. Wastes **28**, 11, 1371, 1956.

[2] LANCY L. E., *The effects of metal finishing effluent on the sanitary sewage treatment processes and sewer structures*, 49th Annual Tech. Proc., American Electroplaters, Society, June, 1962.

[3] GOEBGEN H. G., and BROCKMANN J., *Bindungsvermogen von anaerobem Faulschlamm für Schwermetallionen*, Wasser Luft und Betrieb **13**, 11, 409, 1969.

[4] PAGE A. L., *Fate and effects of trace elements in sewage sludge when applied to agricultural lands*, No. EPA-670/2-74-005, Jan. 1974.

[5] DALTON F. F. and MURPHY R. R., *Land disposal* IV: *Reclamation and recycle*, Journ. WPCF **45**, 7, 1489, 1973.

[6] BERROW M. L., and WEBBER J., *Trace elements in sewage sludges*, Jour. Sci. of Food and Agricult. **23**, 93, 1972.

[7] JOURGENSEN S. E., *Do heavy metals prevent the agricultural use of municipal sludge?* Water Research **9**, 163, 1975.

[8] TULLANDER V., *Final disposal of municipal sludge in Sweden*, Journ. WPCF **47**, 4, 688, 1975.

[9] DEHAAN S., *Land application of liquid municipal wastewater sludges*, Journ. WPCF **47**, 11, 2707–2710.

[10] WEBBER I., *Effects of toxic metals in sewage crops*, Water Pollut. Control (G. B) **71**, 404, 1970.

[11] JOHN M. K., CHUAH H. H. and LAERHOVEN C. J., *Cadmium contamination of soil and its uptake by oats*, Environ. Sci. Techn. **6**, 6, 555, 1972.

[12] JOHN M. K., CHUAH H. H. and VAN LAERHOVEN C. J., *Factors affecting plant uptake and phytotoxicity of cadmium added to soils*, Environ. Sci. Techn. **6**, 12, 1005, 1972.

[13] LAGERWERFF J. V. and SPECHT A. W. *Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc*, Environ. Sci. Techn. **4**, 7, 583, 1970.

[14] CHOWDBURY P. and LOURIA D. B., *Influence of cadmium and other trace metals on human α antitrypsin*, Science **191**, 480, 1976.

[15] KINNISON R. R., *Pb*, Environ. Sci. Techn. **10**, 7, 645–649, 1976.

[16] CRADDOCK J. M., *Muncie Indiana's "Total" Local Water Quality Program*, Water & Sewage Works, June, 1973.

[17] FURR A. K., LAWRENCE A. W. et al., *Multielement and chlorinated hydrocarbon analysis of municipal sewage sludge of American Cities*, Environ. Sci. Techn. **10**, 7, 683–687, 1976.

[18] CRECELIUS E. A. and PIPER D.Z., *Particulate lead contamination recorded in sedimentary cores from lake Washington, Seatle*, Environ. Sci. Techn. **7**, 11, 1053, 1973.

[19] OLIVER B. G., and COSGROVE E. G., *The efficiency of heavy metal removal by a conventional activated sludge treatment plant*, Water Research **8**, 869, 1974.

[20] KLEIN L. A. et al., *Sources of metals in New York City Wastewater*, Journ. WPCF **46**, 12, 2653, 1974.

[21] DAVIS J. A. III and JACKNOW J., *Heavy metals in wastewater in three urban areas*, Journ. WPCF **47**, 9, 2292, 1975.

[22] Anon, *Survery and study for the NCWO, regarding the technology to meet requirements of federal water quality act for the metal finishing industry*, Lancy Div., Dart Envir. and Serv. Co., U. S. Depart. of Commerce NTIS No. P. B. 248–808.

[23] Oliver B. G., *Heavy metal levels of Ottawa and Rideau River Sediments*, Environ. Sci. Techn. **7**, 2, 135, 1973.

[24] Mathis B. J., and Cummings T. F., *Distribution of selected metals in bottom sediments, water clams, tubificid annelids and fishes of the Middle Illinois River*, University of Illinois Water Resources Center, UILU-WRC-71-0041, March, 1971.

[25] Mathis B. J. and Cummings T. F., *Selected metals in sediments, water and biota in the Illinois River*, Journ. WPCF **45**, 7, 1573, 1973.

[26] Pita F. W. and Hyne N. J., *The depositional environment of zinc, lead, and cadmium in reservoir sediments*, Water Research **9**, 8, 701–706, 1975.

[27] Curry N. A., *Municipal sewage sludge disposal*, presented at the N. Y. WPCA Meeting 1976 (Syracuse).

[28] Curry N. A., *Landfilling metal finishing wastewaters sludges*, presented at the AES Mideast Techn. Conference 1976 (May, Clymer, New Jersey).

[29] Sartor J. D., Boyd G. B. and Agardy F. J., *Water pollution aspects of street surface contaminants*, Journ. WPCF **46**, 3, 458, 1974.

[30] Newton C. D., Shephard W. W. and Coleman M. S., *Communication street runoff as a source of lead pollution*, Jour. WPCF **46**, 5, 999, 1974.

[31] Bryan E. H., *Urban stormwater quality and its impact on the receiving system*, Proceedings Twentiech Southern Water Resources Pollution Control Conference, Chapel Hill, N. C., April, 1971.

[32] Bryan E. H., *Communication — concentrations of lead in urban stormwater*, Journ. WPCF **46**, 10, 2419, 1974.

[33] Oliver B. G., Milne C. B. and LaBarre N., *Chloride and lead in urban snow*, Journ. WPCF **46**, 4, 766, 1974.

[34] Guarino C. F., *Land and sea solids management alternatives in Philadelphia*, Journ. WPCF **47**, 11, pp. 2551–2564, 1975.

[35] Davison R. L., Natusch D. F. S., Wallace J. R., Evans C. A. Jr., *Trace elements in fly ash — dependence of concentration on particle size*, Environ Sci. Techn. **8**, 13, 1107, 1974.

[36] Natusch D. F. S. and Wallace J. R., *Urban aerosol toxicity: the influence of particle size*, Science **186**, 695, 1974.

[37] Roberts T. M. et all., *Lead contamination around secondary smelters: estimation of dispersal and accumulation by humans*, Science **186**, 1120, 1974.

[38] Linton R. W., Loh A., Natusch D. F. S., *Surface predominance of trace elements in airborne parti-*cles, Science **191**, 852, 1976.

[39] Klein D. G. and Russell P., *Heavy metals: Fallour around a power plant*, Environ. Sci. Techn. **7**, 4, 357, 1973.

[40] Klein D. H. et al., *Pathways of thirty-seven trace elements through coal-fired power plant*, Environ. Sci. and Techn. **9**, 10, 973, 1975.

[41] Kaakinen J. W. et al., *Trace element behavior in coal-fired power plant*, Environ. Sci. Techn. **9**, 9, 862, 1975.

[42] Gutenmann W. H., Bache C. A. et all., *Selenium in fly ash*, Science 191, 966, 1976.

[43] Campbell W. J., *Metals in the wastes we burn*, Environ. Sci. Techn. **10**, 5, 436–439, 1976.

[44] Olson K. W., Skogerboe R. K., *Identification of soil lead compounds from automotive sources*, Environ. Sci. Techn. **9**, 3, 227, 1975.

[45] Wixson B. G., Jennett J. C., *The new lead belt in the forested ozarks of Missouri*, Environ. Sci. Techn. **9**, 13, 1129–1133, 1976.

[46] Solomon R. L., Hartford J. W., *Lead and cadmium in dusts and soils in a small urban community*, Environ. Sci. Techn. **10**, 8, 773–777, 1976.