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THE SOURCES AND BEHAVIOR OF HEAVY METALS IN WASTEWATER AND SLUDGES

by

B. W. Vigon, R. A. Craig, and N. A. Frazier
BATTELLE
Columbus Laboratories
Columbus, Ohio 43201

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Project Officer

Robert B. Dean
Wastewater Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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16. ABSTRACT

A critical evaluation has been made of the literature regarding the sources of heavy metals in sludges from municipal wastewater treatment plants. Residential loadings of heavy metals as a percentage of total metal loads are highly variable with respect to both the particular element under consideration and the geographic area. Only rarely is the percentage contribution of any metal attributable to residential sources greater than one-half the total. The disagreement between studies seems to indicate that the available information concerning the residential loading estimates may be biased due to the inclusion of unsurveyed industrial discharges. The sludge content of heavy metals is frequently correlated with industrial density, but the many confounding variables make a general statement regarding this relationship impossible. Diffuse sources such as laundries, street runoff and small family-owned operations may contribute to the discharges from a supposedly residential area. Varying proportions of these minor and essentially uncontrollable sources presumably account for the high variability in the available data. The contribution of urban runoff to metal loads of municipal treatment plants is not large relative to other sources at present, because peak flows are usually bypassed. Local studies will have to be made to identify the controllable sources of heavy metals whenever their concentrations in sludge destined for agricultural purposes exceeds acceptable limites because each community has its own unique mixture of industrial and residential sources.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Metals, trace elements, sewage, sludge disposal, land reclamation, land utilization, industrial wastes, copper, zinc, nickel, cadmium, cobalt, chromium, lead, mercury, soil fertility, fertilizers, crops farm crops, forage crops, grain crops, plant nutrients, toxic tolerances, ground water, water quality.	Heavy metals, toxic elements, trace metals, trace inorganics, micronutrients, micro-elements, sewage sludge, sewage effluent, agricultural land, urban wastes, residential wastes, storm drainage.	13B

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The following report is based on a quick literature search and analysis of available data on the respective contributions of industrial and residential areas to heavy metals in sludge produced by sewage treatment plants. Although there is no doubt that high discharges of a heavy metal from an industry will produce a high concentration of that metal in the sludge, reliable data on the relative contributions of industry and residential areas is not available. If heavy metals in industrial discharges are to be regulated to protect crops that will be grown on the sludge, it is reasonable to ask how much of these same metals will be contributed by other sources. This report suggests some of the diffuse sources such as laundries, street runoff and small family-owned operations that may contribute to the discharges from a supposedly residential area. Varying proportions of these minor and essentially uncontrollable sources presumably account for the high variability in the available data. Because each community is unique local studies will have to be made to identify the controllable sources of heavy metals whenever their concentrations in sludge destined for agricultural purposes exceeds acceptable limits.

Francis T. Mayo
Director
Municipal Environmental Research Laboratory

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SUMMARY

The major source of toxic heavy metals to municipal wastewater is a point of controversy. Environmental authorities have proposed pretreatment of industrial wastes prior to entry into the municipal waste stream with the objective of reducing the concentration of these heavy metals in the output of the waste treatment facility. Industry argues that many of these potentially toxic pollutants are ubiquitous so that the major sources of their entry into the municipal waste stream are diffuse and they further argue that control of industrial point sources can therefore result in only marginal reduction in heavy metal concentration in the waste treatment effluent.

A critical examination of the literature to resolve this point of contention indicates several relevant findings. Residential loadings of heavy metals as a percentage of total metal loads are highly variable with respect to both the particular element under consideration and the geographic area. Only rarely is the percentage contribution of any metal attributable to residential sources greater than one-half the total. Furthermore, the maximum quantity of the most troublesome heavy metal, Cd, which might be derived from dietary sources (i.e., excluding pipe leaching and food scraps from garbage disposers) appears miniscule. This fact and the disagreement between studies seems to indicate that the available information concerning the residential loading estimates may be biased due to the inclusion of unsurveyed industrial discharges.

The sludge content of heavy metals is frequently correlated with industrial density, but the many confounding variables make a general statement regarding this relationship impossible. A more promising approach utilizing statistical criteria applied to available data or data obtained in a cursory survey to isolate certain communities or treatment plants for more detailed study could be employed.

Many older communities are served by combined storm and sanitary sewers. The effects of urban runoff associated with rain events is of interest not only for its contribution to the sludge metal content but also for its implications regarding receiving water management. Present indications are that the contribution of urban runoff to metal loads of municipal treatment plants is not large relative to other sources. except perhaps for zinc and lead,

simply because of the common practice of bypassing a large portion of the runoff flow. If, however, future management dictates the detention and treatment of these peak flows, then this source will become a large component of total loading at times.

With respect to the available analyses of the metal content sludges, it appears that the generation of accurate influent concentration data is an impossibility given the present state-of-the-art of modeling the behavior of metals during treatment. Furthermore, insufficient information appears to exist to approach this question in a rigorous manner.

The literature on plant uptake/toxicity indicates that plant uptake of Cd from soils on which sludge is spread generally increases. Studies which do not show this trend are those where low cadmium sludges are spread or where incomplete mass balances are performed. Some empirical evidence exists demonstrating that mechanisms to prevent or delay either the toxic reaction or the uptake of Cd are present. No theoretical data is available to elucidate the nature or stability of this complex. Interspecies variability in the reaction to metal loads is high and present knowledge would dictate selecting crops which do not concentrate the metals in the edible parts or else growing nonfood cash crops.

During the course of this investigation conversations with many knowledgeable persons pointed out the lack of direction in the information gathering and assimilation process. Bits and pieces of data obtained with other objectives in mind often were unusable or did not form a cohesive whole.

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INTRODUCTION

During the past decade, the use of digested municipal sludge as a soil amendment has increased manyfold. The benefits of increased organic content, greater tilth, and larger yields resulting from the application of this material are well documented. However, the nature of the sludging process also results in the retention of heavy metals contained in the original wastewater. Most often the metals in the sludge are highly concentrated relative to that in the raw influent.

Opponents to the use of sludge claim, among other things, that the metals are taken up by plants and spread throughout the food web. Guidelines addressing this issue have met with mixed reviews. Those who feel that adequate natural protective measures exist believe that the present guidelines are overly restrictive and should be relaxed.

In terms of source control to prevent the metals from reaching the sludge, several options are open. Regulations to require the major industrial dischargers to treat and remove the pollutants have been suggested as a possibility. The counter-argument that diffuse sources are major contributors to heavy metal loads has also been put forth. It has been claimed that efforts to reduce metal loads and hence increase allowable sludge application rates because of pretreatment can effect only minimal changes.

Consequently, before an informed policy decision can be made, a critical assessment of the literature on both controllable (industrial) and non-controllable sources (residential and runoff to combined sewers) is warranted. Funding for such an examination has been provided to Battelle by MERL.

RESIDENTIAL CONTRIBUTIONS TO TRACE METAL LOADS

A certain amount of information exists about the contribution of heavy trace metals to treatment plants by residential sewer users. Investigators in New York City[1] studied the metal content of sewage from residential subareas feeding a treatment plant which also services a large industrial population; they also sampled sewage from residential areas in other parts of the city at pumping stations.

Other investigators[2] measured the trace metals content of sewage at six sampling sites in predominantly residential areas of Allegheny County PA (they estimated the nonresidential fraction to be no greater than 10% small commercial establishments.) The latter report also cited the results of measurements by the Muncie (Ind) Division of Water Quality which sampled waste streams receiving no industrial discharges at five sampling stations. These researchers then used this information and other data to infer the relative size of industrial and residential and, in one case, other contributions to the loadings of heavy metals in the waste water.

Reference 2 has accumulated the data on loadings of heavy trace metals for the residential subarea of New York City and the residential areas of Allegheny County Penn. and Muncie, Indiana and displayed them in terms of pounds per day per 1000 persons in the area served. We included their Table 1 but have added a column which includes a weighted average (weighted by average flow) of the data obtained by sampling other residential areas of New York City.

Using this information and other data, the authors of Ref 1 and 2 calculated the fraction of the total wastewater heavy metal loading which could be attributed to residential and industrial sources; these are shown in Tables 2A and 2B, respectively.

TABLE 1. COMPARISON OF RESIDENTIAL METAL LOADING FACTORS

	Residential Loading Factor lb/Day/1000 Persons			
Metal	NY (Bowery Bay)	Allegheny Co.	Muncie	NY (other Resid)
Cd	0.016	0.011	0.006	0.002
Cr	0.08	0.018	0.007	0.018
Cu	0.18	0.10	0.10	0.17
Pb	--	0.062	0.10	--
Ni	0.08	0.012	0.02	0.011
Zn	0.21	0.17	0.21	0.23

TABLE 2A. RESIDENTIAL LOADINGS OF HEAVY TRACE METALS AS A PERCENTAGE OF TOTAL LOADINGS

Metal	NYC	Muncie	Allegheny Co.
Cd	38	--	63
Cr	27	2.7	23
Cu	38	36	96
Pb	--	10	63
Ni	34	13.3	19
Zn	16	17	32
Mn	--	18	--

TABLE 2B. INDUSTRIAL LOADINGS OF HEAVY TRACE METALS AS A PERCENTAGE OF TOTAL LOADINGS

Metal	NYC	Muncie	Allegheny Co.
Cd	39	--	NA
Cr	51	97.7	--
Cu	19	67	--
Pb	--	91.4	--
Ni	65	88.5	--
Zn	20	85	--
Mn	--	75	--

Footnote to Table 2.

The data for Muncie, Ind. as presented in Reference 2 added to more than 100% in some cases. These were taken directly from Reference 2; we believe that these are the result of combined rounding errors.

Examination of the residential loading data thus presented shows that the Zn and Cu loadings are sufficiently close that estimates of baseline residential loadings for these metals of 0.2 and 0.1-0.2 pounds/day/1000 persons, respectively might safely be assumed. Insufficient data is presented about Pb to make any conclusion. The pattern of variation of data for Ni, Cr and Cd suggest that some industrial contribution may inadvertantly have been included in the NY, Bowery Bay data.

The Cd data is particularly interesting as the concentration of this element relative to that for Zn has been identified as a bellwether of industrial input to the waste stream. In addition, because of its toxicity and its ultimate appearance in plants used for human consumption when sludge is used as soil conditioner, an understanding of the sources of this element is a necessity.

The natural level of Cd in drinking water in the NY City area is below the detection limit of the analytical method*; for Allegheny County it was measured to be 0.0025 mg/l in a single measurement (the concentrations of Cu and Zn in NYC tap water are approximately 0.06 mg/l and 0.03 mg/l, respectively; Ref 1 took the concentrations of other metals to be zero in their study). This is not at variance with a national "average" of 1.4 ppb.[4] The accuracy of the EPA standard analysis for Cd used for the Allegheny analysis is quoted as being ± 2 ppb.[3] Assuming this to be the case for the other cities, there is insufficient information to imply Cd loadings above background for Muncie or the other residential areas of NYC.

It is possible to estimate an upper bound to the Cd introduced into the the waste stream as the result of human consumption of foods containing Cd. There is much uncertainty about the threshold of daily dietary intake of Cd to produce kidney dysfunction (after 50 years) but no estimates exceed 1000 μg/day.[4] If everyone consumed foods containing this level of Cd, a sewer loading of 0.002 pounds/day/1000 persons would result. Since chronic cadmium poisoning does not appear widespread, it is safe to assume that the actual daily dietary intake is much smaller; Reference 4 cites an approximate intake of 100 μg/day. Thus, for practical purposes the cadmium ingested in foods can be ignored in attempting to understand the loadings of Cd in residential wastes.

Cadmium does appear as an impurity in zinc; commercial grade Zn contains Cd to the extent of approximately 0.015 percent but can be as much as 0.4 percent. Thus, any cadmium which appears in the wastewater to a greater extent than this has been used as cadmium or has been selectively leached from zinc containing materials (the latter is unlikely as Cd is very similar to Zn and will be expected to leaching a similar manner).

The heavy trace metal percentages attributable to residential sources as given by Reference 1 and 2 seem to be in contradiction with limited data available from other cities. Los Angeles performed a study of metals concentration in wastewater from a single upper middle class residential area. With the caveat that this data may be unrepresentative of residential areas throughout the city, they found the distribution shown in Table 3 by extrapolation to the remainder of the city.[5]

---

* EPA-430/9-75-005.

TABLE 3. SOURCES OF HEAVY METALS TO WASTEWATER IN LOS ANGELES

Metal	Residential Percentage	Industrial/Commercial Percentage
Cd	17	83
Zn	25	75
Cu	13	87
Cr	2	98
Ni	12	88
Ag	45	55

The Chicago data is a bit more indirect. In 1969 the Chicago Metropolitan Sanitary District instituted point source control regulations applicable to industries (primarily platers) which discharged large quantities of heavy metals.[6] The decreases in heavy metal concentration of the sludge for the City of Chicago Calumet Treatment Plant are shown in Table 4.

TABLE 4. REDUCTION IN METAL CONTENT OF SLUDGES OBSERVED AT THE CITY OF CHICAGO-CALUMET PLANT

Metal	Percentage Decrease 1969 - 1974
Cd	72
Cr	62
Cu	81
Hg	35
Ni	92.3
Pb	73
Zn	49

Unfortunately, this data cannot be directly interpreted as implying corresponding decreases in influent concentration of these metals as the waste treatment process was changed in the interim. However, additional data shows that the Zn and Cd loadings of the treatment plant effluent were decreased by the change in treatment process, implying an increased removal efficiency. Thus, the actual decreases in industrial discharge are larger than those indicated in Table 4. Nevertheless, the Chicago data appear to indicate that industrial heavy metal discharges are more important than References 1 and 2 would seem to show; however, Chicago also has a typically high concentration of platers.

It would appear that the most likely source of disagreement in the studies above is the inclusion of the discharge from commercial and small industrial enterprises in the residential discharge component. The NY study(1) indicates that the wastestreams of commercial laundries have large loadings of heavy metals; the study did not describe the source of these heavy metals in commercial laundry effluent, however, these are usually ascribed to the soiled industrial clothing or toweling being cleaned.(7) It would therefore seem reasonable to assume that the effluent from smaller laundries in nearby residential areas, street runoff, and residential effluent may also have wastestreams which reflect the industrial character of the neighborhood. This point deserves further study.

INDUSTRIAL CONTRIBUTIONS TO TRACE METAL LOADS

Use of metals in industry is so widespread as to prevent any meaningful analysis based on the various processes employed. The type and quantity of metal discharges from industries in a given city or area depends on many factors including industrial type, process variables, pollution abatement practices and so forth. The analytical methodology relating to metal quantitation generally measures total metal content. However, some forms of a given metal are so stable that for all practical purposes is unavailable for plant uptake and hence innocuous from a sludge loading standpoint.

Chromium and cadmium are two metals widely used in industrial processes. They have also been the subject of some concern regarding plant and human toxicity effects. In addition some of the environmental chemistry of these elements is known. Major amounts of hexavalent Cr are thought to be associated with the metal plating industry. Cr content of wastes from this industry averaged 41 ppm with each plant discharging approximately 2.5 kg daily. These data are based on information gathered in 1972[8] before much of the recent legislation concerning point source dischargers was enacted. Investigators in Chicago report a 10-12 percent per year decrease in chromium content of sludges over the period 1969-74. Also, a portion of the chromium may be discharged to storm sewers or otherwise not reach the treatment plant. Researchers in New York[1] found that 15 percent was directly discharged without treatment so that a more realistic estimate of the amount reaching the plant might be 1.0 kg per day. This estimate is somewhat in excess of the 0.6 kg obtained in the New York study but probably gives an estimate of the range likely to be encountered.

Industrial sources of chromium are not limited to metal plating. Cr is used as a corrosion inhibitor in cooling towers, in anodizing aluminum in fur dressing, as a tanning agent in the leather industry, in the manufacture of paints, dyes, and explosives. Trivalent Cr is also used in industry, although less commonly. It acts as a mordant in textile dyeing, is used in ceramics and glass, and in photography. Thus, an estimation of the contribution of chromium to waste water from industry must be comprehensive to avoid underestimation. In addition, many small scale operations may be family-owned making a survey difficult.

Besides the New York study, several other investigators[2,9,11] identified industrial contributions of Cr as being significant. In particular, Reference 9 stated the reasons for increasing Cr concentration in sludges as being due to increasing industry to residential ratios, however, no description of the plant type or sewer types was included. The treatment plants were located near Toronto, Ontario, Canada. The Ashbridge Bay plant receives a complex effluent from a heavily urbanized and industrial area (Metropolitan Toronto.) The Thornhill plant receives effluent from a small, basically residential neighborhood possessing a minimum of heavy metal industry. Other industries, not usually thought of as heavy metal industries, may be included. The Aurora plant receives effluent from a large town with a variety of industry, one of which was stated to use chrome extensively. The concentration values show that the metal content (Table 5) is proportional to industrial density except for manganese, iron, and copper which are frequently cited as "residential metals".

The research on chromium also manifests the fact that the form of a metal is tremendously important in determining its environmental significance. The ratio of Cr(VI) to Cr(III) in use is very high but the oxidation/reduction kinetics favor reduction of chromate. This process is thought to take place during secondary treatment[11] and may result in substantial alteration of the toxicity since the trivalent oxidation state is not nearly as hazardous as the hexavalent state.

Industrial uses of cadmium include electroplating, paint, plastic and battery manufacture, alloying, scrap steel and radiator reclamation, and several miscellaneous uses. Cadmium is also found as a trace contaminant in zinc ores and since the separation is relatively costly, may be indirectly discharged as a result of industrial zinc processing. An examination of 1,123 samples of industrial wastes of the Chicago area indicated that 1.4 percent contained more than 10 mg/l Cd and 0.27 percent contained more than 50 mg/l; all these were from metal treatment and plating.[10] Data from the Chicago area[6] also indicate that the cadmium in sludges from plants serving the central city is much higher than in sludges from outlying suburban areas even though the same level of treatment is employed. While certainly not conclusive, this suggests that treatment plants in

TABLE 5. METALS ANALYSIS OF SLUDGE SAMPLES FROM DOMESTIC STP'S NEAR TORONTO, CANADA[a]

Plant	Cr	Zn	Fe	Cu	Mn	Ni	Pb	Cd
	Percent				ppm			
Aurora	1.6	0.94	0.7	0.03	260	120	235	10
Thornhill	0.006	0.11	0.9	0.24	450	25	185	5
Ashbridges Bay	0.43	0.58	1.5	0.11	280	170	1425	45

Reference 9.

residential suburban areas exhibit how cadmium levels because of the lack of industry. However, many newer suburban areas also have separate sewer systems in contrast to the combined systems in older central city neighborhoods. Roughly the same correlation exists for Wisconsin communities; those with known industrial activity show high cadmium levels in the sludge.[6] The same trend is evident in the data from Reference 9.

RUNOFF AS A SOURCE OF METALS IN STP INFLUENT

Some portion of metals in runoff from sewered areas serviced by combined sewers can appear in STP sludges destined for land spreading. Examined in this section are examples of data bearing on sources and quantities of metals accessible to or in runoff from urban areas.

Over the past few years, a considerable body of information on metals in runoff has been developed. By and large, however, this information pertains mostly to degradation of the body of water receiving the runoff directly from storm sewers and surface drainage channels rather than to runoff as an influent to an STP.

Metals in Street Dirt

During dry weather, dirt accumulates on streets. Sources of dirt include dirt fallout, dirt on vehicles and their tires, and particulates from industrial emissions and vehicular exhausts. For urban areas served by combined sewers, street runoff can be a source of metals in an STP influent. The size of this source depends on the capacity of the treatment plant. Recent studies[12,13] have developed information on metals associated with street dirt in several U.S. cities. For example, shown in Table 6 are data on selected metals in dirt samples from urban residential, industrial, and commercial streets.

The amount of metals in street dirt which may end up in STP sludge depends upon several factors. These include land use, the rate and distribution of precipitation, the rate at which street dirt accumulates, STP treatment processes and hydraulic capacity, the strength or concentration of metals in street dirt, and particle size of solids with which metals are associated. Data on accumulation rates and particle size distribution are shown in Table 7. Referring to Part A of Table 7, two items are noteworthy: (1) lead and zinc accumulate an order of magnitude more rapidly than the other metals listed, and (2) the wide variability in accumulation rates.

Part B of Table 7 shows the size distribution of the solids for each metal species. If one is interested in removing cadmium by street

TABLE 6. ELEMENTAL COMPOSITION OF STREET CONTAMINANTS[a]

Element	Residential	Industrial	Commercial	Residential	Industrial	Commercial
	mg/kg[b]			lb/curb mi		
Beryllium	0.2	2	0.2	<.001	.006	<.001
Cadmium	<2	<2	<2	<.002	<.006	<.001
Chromium	200	500	100	.24	1.4	.029
Copper	100	100	100	.12	.28	.029
Lead	2,000	5,000	5,000	2.4	14	1.4
Mercury	<1	<1	<1	<.001	.003	<.001
Nickel	100	100	50	.12	.28	.015
Zinc	100	100	100	.12	.28	.029

(a) Reference 13.

(b) To convert from mg/kg solids to lb/curb mile, multiply by the amount of street solids per curb mile. Note that the time rate of accumulation (lb/curb mile/day) is different for each element (see Table 7).

TABLE 7. STREET DIRT: METAL ACCUMULATION RATES AND PARTICLE SIZE DISTRIBUTION

	A. Accumulation Rates[a] (lbs/curb mi/day)		B. % Distribution by Particle Size[b] of Street Solids[c] (Each species = 100%)				
	Numerical Mean (m)	Avg. Deviation ÷ m	<104	104 to 246	246 to 495	>495	Total
Cd	0.0014	0.86	36%	52%	12%	0%	100%
Cr	0.050	0.54	20	24	17	39	100
Cu	0.15	1.2	26	33	15	26	100
Hg	0.016	0.31					
Pb	0.38	1.2	23	17	31	29	100
Ni	0.018	0.33	14	28	35	23	100
Sr			34	12	15	39	100
Zn	0.53	1.2	20	26	21	33	100
Solids	700	0.89					

	C. Accumulation Rates versus Particle Size[b] of Solids (lbs/curb mi/day)[d]					D. % Distribution by Particle Size[b] of Street Solids[e] (Sum of species = 100%)				
	<104	104 to 246	246 to 495	>495	Total	<104	104 to 246	246 to 495	>495	Total
Cd	0.050	0.073	0.017	0	0.14	0.05%	0.06%	1.49%	0%	1.6%
Cr	1.0	1.2	0.85	1.95	5.0	0.89	1.06	0.75	1.73	4.43
Cu	3.9	4.95	2.25	3.9	15	3.45	4.38	1.99	3.45	13.27
Hg										
Pb	5.32	10.64	13.3	8.74	38	4.71	9.42	11.78	7.74	33.65
Ni	0.41	0.31	0.56	0.52	1.8	0.37	0.27	0.49	0.46	1.59
Sr										
Zn	10.6	13.78	11.13	17.49	53	9.38	12.2	9.85	15.49	46.92
Total (Approx.)	21.28	30.95	28.10	32.60	112.94	18.85	27.39	26.35	28.87	100

(a) From Reference (12). Samples from 4 U.S. cities collected from 1 to 13 days following a rain or sweeping of street.
(b) Microns
(c) From Reference (13). Samples from 4 U.S. cities, 2 of which are included in "A".
(d) Computed from "A" and "B". All values have been multiplied by 100.
(e) Computed from "B".

sweeping or by runoff retention basins, then Part B suggests that street solids in the 104 to 206 micron range contain the majority of cadmium. It is interesting to note that highest percentages of cadmium and zinc are associated with different particle sizes.

In Part D of Table 7 the sum of Cd, Cr, Cu, Pb, and Zn present in street dirt was set equal to 100 percent and the distribution by particle size computed. If these five metals as a group were of interest, these data suggest that they are present in about equal amounts in the 104 to 246, 246 to 495, and greater than 495 micron particle size categories.

Street runoff from rain or snow with sufficient velocity to transport street solids, if not bypassed or collected in runoff retention basins for subsequent release to an STP, is an additional hydraulic load to an STP. During wet weather the volume of the runoff can decrease concentrations of metals in an STP influent, although metal loading rates as well as total metal loads are increased. On the basis of the hypothetical city described in Table 8, metal loading from street runoff has been calculated and compared to normal sanitary sewage[12] (see Tables 9 and 10). Metal loadings from street runoff were computed using overall averages for street dirt; data on sanitary sewage metals are based on records from two California sewage treatment plants.

There is evidence (e.g., References 13, 14, and 15) showing an increase in Pb, Zn, Cd, and Ni concentration in surface soils with increasing proximity to highways with the contamination being related to composition of gasoline, motor oil, and tires. Analysis[16] of soils from 65 sampling stations at street intersections in a large Canadian city revealed substantially higher lead and zinc concentrations in the top 2.5 cm soil layer than in the soil at depths between 10 and 15 cm (see Table 11). The top layer also had higher concentrations of As, Cd, Cu, and Ni than the lower layer.

On the more general topic of urban runoff, data on concentrations of Cu, Pb, and Zn at various depths in the soils of storm drainage retention basins are given in Table 12. Note the much higher concentration of Pb and Zn and to a lesser extent of Cu in the depth interval of 0-5 cm.

TABLE 8. HYPOTHETICAL CITY PARAMETERS[12]

Population:		100,000 people
Total land area:		14,000 acres
Land-use distribution:		
Residential	75%	
Commercial	5%	
Industrial	20%	
Total street lengths:		400 curb miles
Sanitary sewage flow:		12 MGD

TABLE 9. METAL LOADING FROM ROAD SURFACE RUNOFF COMPARED TO NORMAL SANITARY SEWAGE*[12]

METAL	ROAD RUNOFF (lb/hr)	SANITARY SEWAGE (lb/hr)	RATIO: RUNOFF / SANITARY
Lead	600	0.13	4,600
Cadmium	1.2	0.0032	380
Nickel	10	0.042	240
Copper	36	0.17	210
Zinc	140	0.84	170
Iron	7,900	54	150
Manganese	150	9.7	15
Chromium	80	12	6.7

* "Hypothetical City" with 0.1 in. rain, lasting for one hour.

TABLE 10. METAL LOADING FROM ROAD SURFACE RUNOFF COMPARED TO NORMAL SANITARY SEWAGE FLOW[12]

METAL	ROAD RUNOFF (mg/l)	SANITARY SEWAGE (mg/l)	RUNOFF / SEWAGE
Pb	6.2	0.03	210
Cd	0.012	0.00075	16
Ni	0.10	0.01	10
Cu	0.37	0.04	9
Zn	1.4	0.20	7
Fe	83	13	6
Mn	1.6	2.3	0.7
Cr	0.80	2.8	0.3

(from 0.1 in. rain)

TABLE 11. AVERAGE CONCENTRATION OF METALS IN SOILS FROM 65 SAMPLING STATIONS IN A LARGE METROPOLITAN AREA[13] (ppm)

	Depth 0-2.5 cm	Depth 10-15 cm
As	8.4	8.2
Cd	2.3	2.1
Cu	33.2	30.9
Ni	34.8	30.3
Pb	292	148
Zn	154	115

Note: Sampling stations at major street intersections in a southern Ontario city with population of over 2 million.

TABLE 12. METALS IN SOILS IN URBAN STORM RUNOFF RETENTION BASINS[14] (mg/kg)[d]

Basins[a]	Depth Below Soil Surface (cm)	Copper Arith. Mean	Copper SD: % of Mean	Copper Median	Lead Arith. Mean	Lead SD: % of Mean	Lead Median	Zinc Arith. Mean	Zinc SD: % of Mean	Zinc Median
12 Storm	0-5	19.9	13.6	17	224.8	25.0	165	107.9	24.7	78
Drainage	5-15	10.7	7.5	11	25.4	14.6	21	38.6	9.6	37
Retention[b]	15-30	10.8	9.3	16	17.0	9.4	16	35.5	7.6	35
4 "Control" Basins[c]	0-30	17.5	16.0	15	16.5	9.1	15	36.2	11.6	36

(a) Fresno Metropolitan Flood Control District, Fresno, Calif.
(b) Year basins began receiving runoff ranges from 1962-1971. Grasses planted in some of the basins.
(c) Three of the 4 control basins had been recently excavated and had not yet received any urban runoff. The fourth was further excavated and a new soil profile was exposed.
(d) Soil profiles obtained by auger.

Calling attention to problems of disposal of waste products (in this case, acidic industrial wastes) Korte, et al.,[17] analyzed 10 soils from seven states for total metals present and then determined the percent of total metals leached by an acidic solution (see Table 13). Location of the soil samples was not given, but since Pb was present in only barely detectable amounts, samples were presumably from rural areas or at least at some distance from heavily traveled highways. These data are included here because (1) they show the amounts of metals that can be present in soils (and therefore runoff) and (2) they shed light on the more general but related topic of the relative mobility of metals. The order of the relative amount (as a percentage of the total) of a metal eluted was:

$$Mn \gg Co > Ni \simeq Zn \gg Cu \simeq Cr > Pb \simeq Cd.$$

Urban Runoff

Among the studies to determine the characteristics of urban runoff is that of Colston[18] on the Third Fork Creek 1.67 square-mile drainage basin in Durham, North Carolina. A total of 521 samples were taken from subbasins during 36 separate runoff events. Shown in Table 14 are the mean, standard deviation, and ranges in concentration of metals for all storm samples from the basin. Regression analysis showed the significant independent variables affecting stormwater quality to be the rate of discharge and the time from storm start as indicated by the initiation of runoff. Elapsed time since the last storm was found not to be a significant factor. A first-flush effect was apparent from a tendency for concentrations to increase with an increase in rate of runoff and then decrease as time from storm start increased. A conclusion of the study was that urban runoff quality did not exhibit significant variations attributable to land use in the various subbasins. However, other investigators[19, 20] have noted a variation in pollutant loads with land use. Metal concentrations in storm flow from the subbasins and land use characteristics of the subbasins are shown in Table 15.

Of primary interest to this study is the comparison of annual yield of metals/acre of Third Fork Creek drainage basin in raw municipal

TABLE 13. TOTAL ANALYSIS AND ELUTION OF TRACE METAL IN SOILS(7)

Total Analysis of Trace Metals (a) μg/g

State Soil Order	Ariz Enti-sol	Ariz Alfi-sol	Ariz Aridi-sol	Haw Oxi-sol	Ill Alfi-sol	Ind Molli-sol	Ky Alfi-sol	Mich Spade-sol	NC Ulti-sol	NC Ulti-sol
Co	50	45	50	310	50	60	30	25	120	--
Cr	25	38	18	410	55	68	68	15	90	--
Cu	200	60	265	260	80	83	65	46	160	62
Mn	275	280	825	7400	360	330	950	80	4100	50
Ni	80	100	100	600	110	130	135	50	120	80
Zn	55	70	85	320	77	100	130	45	110	40
Sand %	71.3	34.8	52.4	23.0	9.5	6.9	3.0	91.4	19.0	87.9
Silt %	13.7	18.8	37.1	25.0	59.8	58.2	47.1	3.9	19.7	8.3
Clay %	15.0	46.4	10.5	52.0	30.7	34.9	49.1	4.7	61.3	3.8

Note: Most soils yielded traces of Cd and Pb, but irregularly and only in barely detectable amounts.

(a) 1 ml of aqua regia and 6 ml of HF used for 0.1g sample size. After digestion 2.0g of boric acid added and sample diluted to final volume of 50 ml.

Percent of Total Analysis and Peak Concentration of Metal Eluted(b)

Co	% eluted	2.2	1.3	4.4	33	3.2	33	84	7	30	(c)
	peak ppm	2.0	0.6	2.2	26	2.1	3.8	4.7	1.7	11	0.3
Cr	% eluted	(c)	(c)	(c)	1	(c)	0.2	(c)	(c)	6	(c)
	peak ppm	(c)	(c)	(c)	1.8	(c)	0.1	(c)	(c)	2.8	(c)
Cu	% eluted	0.4	(c)	(c)	13	0.9	0.2	(c)	(c)	1.6	0.3
	peak ppm	0.7	(c)	(c)	8.4	0.7	0.2	(c)	(c)	0.9	(c)
Mn	% eluted	41	27	25	59	6.4	(d)	36	9	68	12
	peak ppm	220	40	225	1400	23	375	148	6	950	18
Ni	% eluted	1.5	1.8	2.2	24	0.8	6	5	1.6	2.3	1.4
	peak ppm	1.5	0.6	1.3	34	1.0	3.6	1.8	(c)	0.7	0.02
Zn	% eluted	1.8	2.3	0.7	14	1	2	38	7.3	2.2	1.5
	peak ppm	1.3	0.6	0.2	13	1.0	0.9	1.6	8.6	0.6	0.4

(b) Column effluents. Leaching solution consisted of 0.025M $AlCl_3$, 0.025M $FeCl_2$, and enough HCl to obtain pH of 3. Columns leached until effluent concentration of Fe and Al equalled that of influent.

(c) None of element detected.

(d) Some samples were lost.

TABLE 14. AVERAGE, RANGE, AND STANDARD DEVIATION OF METAL CONCENTRATIONS FOR ALL STORM SAMPLES: THIRD FORK CREEK DRAINAGE BASIN, DURHAM, NORTH CAROLINA

	Mean mg/l	Standard deviation	Range (mg/l) Low	High
(Total Solids)	1440	1270	194	8620
(Total Suspended Solids)	1223	1213	27	7340
Aluminum	16	8.15	6	35.7
Calcium	4.8	5.6	1.1	31
Cobalt	.16	.11	.04	.47
Chromium	.23	.10	.06	.47
Copper	.15	.09	.04	.50
Iron	12	9.1	1.3	58.7
Lead	.46	.38	0.1	2.86
Magnesium	10	4.0	3.6	24
Manganese	.67	.42	.12	3.2
Nickel	.15	.05	.09	.29
Zinc	.36	.37	.09	4.6

TABLE 15. METAL CONCENTRATIONS IN BASE STREAM FLOW AND URBAN RUNOFF FROM SUBBASINS IN THE THIRD FORK CREEK DRAINAGE BASIN, DURHAM, NORTH CAROLINA[18]

	Sub-Basin						
	E-1	E-2	N-1	N-2	W-1	W-2	Total Basin
	Land Use Characterization						
% of Total Acres[a]	5.2	24.6	17.1	17.9	15.8	19.4	100
Population Density/Acre	13.5	6.9	3.8	1.5	3.5	10.8	6.0
Stream Length (ft)	1312	3221	3350	3484	3282	2610	----
Land (%)							
Residential	100	50	63	18	85	73	59
Commercial	0	36	8	44	0	4	19
Public/Institutional	0	9	19	13	15	9	12
Unused	0	5	10	25	0	14	10
Surface Characteristics (%)							
Paved	5	27	16	33	16	11	20
Roof Tops	7	13	5	12	5	9	9
Unpaved Streets	12	3	1	1	3	6	3
Vegetation	76	57	78	54	77	74	68
	Average Base Flow Concentrations (mg/l)						
Total Solids	358	392		428	250	289	400
Suspended Solids	82	20		25	20	24	50
Co	0.10	0.15		0.10	0.13	0.17	0.26
Cr	0.25	0.21		0.30	0.23	0.26	0.23
Cu	0.10	0.16		0.14	0.11	0.14	0.27
Fe	2.3	1.4		1.4	1.2	2.8	1.5
Mg	13.4	17.7		11.2	11.4	12.4	11.8
Mn	1.3	0.50		0.47	0.42	0.40	0.52
Ni	0.19	0.15		0.17	0.19	0.20	0.16
Pb	0.27	0.24		0.21	0.18	0.19	0.26
Zn	0.13	0.15		0.51		0.11	0.16
	Average Concentrations During Storm Flows (mg/l)						
Total Solids	834	849		977	819	938	1440
Suspended Solids	627	638		770	629	739	1223
Al	27	23		22	18	23	16
Co	<0.1	0.1		<0.1	<0.1	<0.1	0.16
Cr	0.13	0.15		0.16	0.13	0.15	0.23
Cu	0.11	0.13		0.12	0.10	0.12	0.15
Fe	10	6		5	10	13	12
Mg	16	10		10	7.5	11	10
Mn	0.84	0.49		0.51	1.1	0.52	0.67
Ni	<0.01	<0.1		<0.1	<0.1	<0.1	0.15
Pb	0.26	0.13		0.32	0.27	0.25	0.46
Sr	<0.1	<0.1		<0.1	<0.1	0.11	
Zn	0.22	0.32		0.27	0.32	0.23	0.36

(a) 1069 Acres

TABLE 16. COMPARISON OF METALS IN RAW MUNICIPAL WASTE AND URBAN RUNOFF FOR NORTH CREEK DRAINAGE BASIN, DURHAM, N.C.[18] (lbs/acre/year yield)

Metal	Raw Municipal Waste		Urban Runoff		Total[a]
	lbs	% of Total	lbs	% of Total	lbs
Chromium	0.10	5	1.3	76	1.7
Copper	0.20	6	1.2	67	1.8
Lead	<.8	11	2.5	68	3.7
Nickel	<.16	21	1.0	77	6.3
Zinc	1.5	43	1.8	51	3.5

(a) Includes metals in base flow of stream; see Table 15.

Note: 100% - (Raw waste % + urban runoff %) = % of total for base flow.

waste and urban runoff (see Table 15). Although runoff in the basin flows to the headwaters of Third Fork Creek, data in Table 16 indicate that if the runoff were a part of the STP influent, metal loads for the species indicated would be roughly an order of magnitude greater from runoff than from municipal waste with the exception of zinc.

Klein, et al.,[1] conducted a mass balance study on metals from various sources in New York City treatment plant influent. Using average concentrations of metals in 35 grab samples obtained from several surface areas during rains and estimating the portion of annual runoff reaching the sewage treatment plants at 95 MGD, the results obtained are shown below in Table 17.

TABLE 17. AVERAGE DAILY METAL LOADS IN NEW YORK CITY STP INFLUENT FROM URBAN RUNOFF[1] (Based on Annual Runoff)

	Concentration (mg/l)	Runoff Load (lb)	Percent of Total Load
Cd	0.025	19	12
Cu	0.46	360	14
Cr	0.16	135	9
Ni	0.15	110	10
Zn	1.6	1220	31

Data on metals from nonrunoff sources determined by Klein, et al.,[1] are given elsewhere in this report. Their results pertaining to runoff are based on metals on 35 grab samples and whether or not their values actually reflect a first-flush concentration or a time and flow weighted concentration of metals in the runoff is one of the main unknowns in their results. In any event, their approach to determine the mass balance from nonindustrial as well as industrial sources represents the type of work that is sorely needed in cities served by combined sewers for evaluating the need for and effectiveness of industrial pretreatment as a means of reducing metals in sludges.

THE BEHAVIOR OF HEAVY METALS DURING WASTEWATER TREATMENT

The treatment of municipal and/or industrial wastes involves a series of unit processes each of which is capable of reducing the oxygen demand or solids content of the water and producing a stable, disposable sludge. The sequence of steps and the nature of the physical, chemical, or biological process involved determines the degree of volatile solids destruction, the sedimentation of fixed solids and, not incidentally, the fate of trace metals.

The identification of the behavior of heavy metals during the treatment process has been acknowledged as a serious need for over 15 years. The use of treated sludge as a soil amendatory agent has also become more prevalent and consequently has created new impetus to quantitate the amounts of heavy metals and determine their physical and chemical characteristics. Until recently, it was nearly impossible to perform valid analyses on any component of the treatment except the sludge due to the lack of requisite sensitivities of the laboratory procedures. Routine determination of metals at the parts-per-billion level were and continue to be beyond the capabilities of most laboratories. This situation has resulted in the compilation of a wealth of data on the concentrations of heavy metals in dried digested sludges but very little information on inflow concentrations. A typical comment regarding the extrapolation of these data to the influent concentrations is that the sludge concentrations generally reflect the influent values. Such statements sound deceptively accurate. It is easy to visualize a nearly linear relationship between loading of a metal to a municipal sewage treatment plant (STP) and the metal content of a sludge. However, several lines of evidence suggest that attempts to determine influent concentrations from sludge values will produce erroneous estimates in the majority of cases.

One technique for estimation of influent concentrations involves the calculation of the mass of sludge solids resulting from treatment of a given volume of wastewater.[21] Another way of visualizing this type of data analysis is to realize that the sludging process is a combination of volume reduction and partition equilibrium. In order to calculate the influent concentration, three parameters must be evaluated, namely, the amount of sludge created per unit volume of wastewater, the chemical or electrostatic partition coefficient (generally defined simply as a percentage removal), and the concentration of metal in the sludge. The mathematical expression takes the form of a mass balance:

Metal in influent = Metal in effluent + metal in sludge

or

$$V_1X = V_2Y + GZ$$

where:

V = Volumetric basis ($V_1 \approx V_2$); usually taken as 1 liter
X = Concentration of metal in influent
Y = Concentration of metal in effluent
G = Amount of sludge generated per unit volume of wastewater treated
Z = Concentration of metal in sludge on a dry weight basis.

This formulation is accurate to the degree that the amount of sludge generated is known or can be calculated. For each type of treatment scheme, a sludge generation factor must be determined. In addition, V_2Y is often also unknown, but an assessment of similar treatment schemes or previously gathered data may permit estimation of the efficiency of removal: $\frac{V_2Y}{V_1X}$.

Concentration data[6] for four metals, copper, zinc, nickel, and cadmium, were used to tabulate the central tendency and dispersion. Sampling, analysis, and compositing methodology is unknown. In order to observe the magnitude of error associated with such data reduction, the concentration ratios were calculated; the appropriate log-normal statistics are shown (Table 18). The spread factors are not unusual for this type of population. The correlation coefficients for the concentration ratios (Table 19) show that only in the case of nickel is the pickup by the sludge significantly and positively related to the influent concentration. Using the sludge generation factor cited by Reference 22 and the median removal efficiencies, it was possible to estimate influent concentrations of these four metals to a number of American cities based on sludge concentrations supplied in Reference 23. These estimates (Table 20) are well within the observed range for Wisconsin STP's.

TABLE 18 . LOG-NORMAL STATISTICS FOR HEAVY METAL CONCENTRATION RATIOS IN 35 WISCONSIN TREATMENT PLANTS[a][b]

Metal	Parameter	
Cu	Geometric mean	6392
	Spread factor	2.57
	95% Confidence limits	968-42,218
Zn	Geometric mean	5567
	Spread factor	2.21
	95% Confidence limits	1140-27,190
Ni	Geometric mean	1799
	Spread factor	2.50
	95% Confidence limits	288-11,244
Cd	Geometric mean	1141
	Spread factor	2.94
	95% Confidence limits	132-9,862

(a) Reference 6.

(b) Concentration ratio = concentration in sludge / influent concentration.

TABLE 19. CORRELATION BETWEEN INFLUENT METAL CONCENTRATION AND SLUDGE CONCENTRATION[a]

Metal	r
Copper	-0.731
Zinc	0.216
Cadmium	0.372
Nickel	0.996

(a) Reference 6

TABLE 20. PREDICTED INFLUENT CONCENTRATIONS OF HEAVY METALS TO TREATMENT PLANTS FOR AMERICAN CITIES [(a)]

City	Cadmium	Nickel	Zinc	Copper
Atlanta, GA	0.01	0.18	0.51	0.22
Cayuga Heights, NY	<0.005	0.04	0.10	0.13
Chicago, IL	0.005	0.06	0.21	0.09
Denver, CO	0.006	0.60	0.51	0.21
Houston, TX	0.014	0.11	0.46	0.24
Ithaca, NY	0.008	0.18	0.30	0.20
Los Angeles, CA	0.02	0.43	0.82	0.44
Miami, FL	0.02	0.49	0.25	0.18
Milwaukee, WI	0.06	0.39	0.24	0.20
New York, NY	<0.005	0.15	0.24	0.29
Philadelphia, PA	0.03	0.46	1.23	0.41
San Francisco, CA	<0.005	0.24	0.11	0.14
Schenectady, NY	<0.005	0.08	0.19	0.14
Seattle, WA	0.009	0.16	0.32	0.18
Syracuse, NY	0.02	0.23	0.33	0.16
Washington, D.C.	<0.005	--	0.26	0.07

(a) From Reference 23, Concentrations in mg/l.

The only city for which direct comparison with the data in Reference 6 is possible is Milwaukee. The measured and estimated values are shown in Table 21. Since Milwaukee has several plants and since this reference did not state which plant was sampled, data for the two surveyed are given. Additional information concerning the service area and facility would be useful in determining the independent variables influencing the pickup process. One point worth noting is that a number of the plants apparently achieved negative efficiencies. Whether this is due to recycling of anaerobic digester supernatant coupled with a poor analysis scheme or to contamination from piping or tanks is not known.

It is felt that log-normal statistics also could be used to select areas for further more detailed study. This mode of analysis has been used to treat the information on metals in Wisconsin STP's (Table 22). It is apparent that not all of the plants exceeding the 95 percent confidence interval do so at all three measurement points. Also of interest is the fact that the cities noted as being out of range are different for each metal (Table 23).

The results of some limited research to correlate the efficiency of metal removal with the type of treatment practiced at a given plant have been published. One study[11] routinely monitored the efficiency of heavy metals removal in six STP's in midwestern cities. Four basic plant types were included:

(1) Primary with sludge digestion

(2) Primary with vacuum sludge filtration

(3) Trickling filter secondary with sludge digestion

(4) Activated sludge secondary with sludge digestion.

None of the sludges from these plants is landspread so no digested sludge samples were analyzed. Influent, final effluent, and primary sludge composited samples were collected from all plants and secondary sludge samples from those plants practicing secondary treatment. Compositing was performed over a 2-week period taking flow variations into consideration so that diurnal variability should be partly averaged. There appears to be little correlation between heavy metal removals and plant size or population served. A recalculation of data supplied by these authors did show a slight ($r = 0.562$; $P < 0.15$) correlation between percent metal

TABLE 21. COMPARISON OF PREDICTED AND MEASURED VALUES OF METALS INFLUENT TO THE MILWAUKEE, WISCONSIN TREATMENT PLANTS

Metal	Predicted Concentration[a]	Measured Concentration, mg/l	
		Jones Is.	South Shore
Cu	0.20	0.07	0.48
Zn	0.24	1.00	0.68
Ni	0.39	0.12	0.20
Cd	0.06	0.06	<0.02

TABLE 22 . LOG-NORMAL STATISTICS FOR 35 WISCONSIN TREATMENT PLANTS [a]

Metal	Parameter	Influent	Effluent	Sludge
Cu	Geometric Mean [b]	0.10	0.06	696
	Spread Factor	2.62	2.20	2.48
	95% Confidence Limits [b]	0.01-0.69	0.01-0.29	113-4281
Zn	Geometric Mean	0.42	0.19	2332
	Spread Factor	2.11	2.45	2.04
	95% Confidence Limits	0.09-1.87	0.03-1.14	560-9705
Ni	Geometric Mean	0.10	0.09	111
	Spread Factor	2.68	2.44	5.06
	95% Confidence Limits	0.01-0.72	0.02-0.53	4.33-2842
Cd	Geometric Mean	<0.02	0.01	30
	Spread Factor	2.01	1.75	3.23
	95% Confidence Limits	<0.005-0.08	0.003-0.03	2.78-312

(a) Data from Reference 6

(b) Means and Confidence Limits in Parts Per Million

TABLE 23. WISCONSIN STP'S EXHIBITING ABNORMALLY HIGH OR LOW HEAVY METAL CONCENTRATIONS[a]

Plant	Metal	Sample Point	Exceeded Limits on Low or High Side of Distribution[b]
Eau Claire	Cu	Influent, effluent, sludge	High
LaCrosse	Cu	Effluent	High
Milwaukee (South Shore)	Cu	Effluent	High
Neenah	Zn	Sludge	Low
Waukesha	Zn	Sludge	High
No. Fond du Lac	Ni	Influent, effluent sludge	High
Wisconsin Rapids	Ni	Effluent	High
Fond du Lac	Cd	Influent, effluent	High
Ripon	Cd	Influent, effluent	High
LaCrosse	Cd	Effluent	High
West Bend	Cd	Sludge	High

(a) Reference 6
(b) Based on 95% confidence limits; n = 35.

removal and total metal loadings. However, analysis of the relationship between removal efficiency and the influent concentration of a particular metal showed no consistent trend (Table 24). The correlation coefficients for two of the metals, copper and zinc, were highly positive in accord with these authors' original contentions. The coefficients for cadmium and mercury are slightly significant and positive; that for lead is insignificant. The correlation of chromium concentration with removal is slightly significant and negative! By averaging the data these investigators obscured the differences in behavior between the metals.

It was claimed that the secondary treatment plants achieved higher removal percentages possibly because of the adsorption of the metals onto the biological floc. Without disagreeing with these conclusions, it would be more defensible to suggest a mechanism for the removal process by performing additional studies of a theoretical nature. Calculations of the solubility of metal hydroxides[22] showed that if a solid phase was present it alone could reduce dissolved Cu^{2+}, Pb^{2+}, and Cr^{3+} concentrations to approximately 1 mg/l. However, no soluble complexes other than hydroxides were considered. The competition of other ligands for the metal ion and the effect of the presence of other solid phases thermodynamically stable in the pH range 6.5 - 9 were also not examined. Considerations of solid metal carbonates, oxides or mixed anion complexes could alter the solubility relations substantially. The effects of organic chelators on the solubility of trace heavy metals has been noted[22,23] but not examined in this context. Likewise little theoretical evidence was provided for attributing the generally higher removal for STP's practicing secondary treatment to an adsorption mechanism on the microbial floc formed during the activated sludge process. The observation of higher removals during secondary treatment has been noted by other authors as well[22,24,25].

Reference 26 attempted to show differences between primary and secondary plants by means of a cumulative frequency distribution. The data (Table 25) indicates first that in order to make valid statements about the relationships between influent and sludge concentrations, more sensitive analytical methods must be employed. For example, the true median cadmium concentration may be only slightly less than the detection

TABLE 24. CORRELATION BETWEEN INFLUENT METAL CONCENTRATIONS AND REMOVAL EFFICIENCY[(a)]

Metal	r
Pb	0.189
Cu	0.817
Cd	0.379
Cr	-0.355
Zn	0.780
Hg	0.542
Total Metal Concentration	0.562[(b)]

(a) Data from Reference 11.

(b) Author's' value is 0.945.

TABLE 25. COMPARISON OF MEDIAN AND 95TH PERCENTILE CONCENTRATIONS AND REMOVAL EFFICIENCIES FOR TREATMENT PLANTS IN THE INTERSTATE SANITATION DISTRICT HAVING PRIMARY AND SECONDARY TREATMENT [(a)]

Metal	Plant Type	Median Concentration Influent	Median Concentration Effluent	Percent Removal	95th Percentile Influent	95th Percentile Effluent	Percent Removal
Copper	Primary	0.10	0.10	0	1.15	0.65	44
	Secondary	0.10	0.05	50	0.40	0.25	38
Zinc	Primary	0.20	0.18	10	1.56	1.42	9
	Secondary	0.16	0.08	50	0.54	0.26	52
Chromium	Primary	<0.05	<0.05	--	0.50	0.45	10
	Secondary	<0.05	<0.05	--	0.35	0.15	57
Lead	Primary	<0.20	<0.20	--	0.60	0.40	33
	Secondary	<0.20	<0.20	--	<0.20	<0.20	--
Nickel	Primary	<0.10	<0.10	--	0.60	0.50	17
	Secondary	<0.10	<0.10	--	0.30	0.20	33
Cadmium	Primary	<0.02	<0.02	--	0.04	0.06	--
	Secondary	<0.02	<0.02	--	0.02	0.02	0
Mercury	Primary	0.0012	0.0009	25	0.0088	0.0100	--
	Secondary	0.0013	0.0009	31	0.0080	0.0059	25

(a) Reference 26 Concentrations in mg/l.

limit. In this case a concentration factor of only about 500 would cause the cadmium concentration in the sludge to exceed the 10 mg/kg guideline for land application. Secondly, it was stated that primary treatment plants achieved poorer removal of heavy metals. Clearly, this statement cannot be supported statistically for the median concentrations of all the metals listed except copper and zinc. These authors also stated that the primary plants served largely industrial users while secondary plants received predominantly residential contributions and only a small amount of industrial waste (percentage not estimated). At the median concentration there is little difference between the influent concentrations of any of the metals. This indicates that the majority of industrial users are not discharging high concentrations of heavy metals, that the concentrations discharged by the industrial contributors to the secondary plants are very high, or that only some (<50 percent) of the primary plants are dominantly industrial. At the 95th percentile, all metals demonstrated higher influent concentrations in the primary plants suggesting that a relatively few plants served industries who were discharging metals (assuming that the original relationship between primary plants and industry is valid and that primary plants serve areas which have approximately the same quality of residential or urban contributions). In fact, this last condition may not be met for heavily industrialized areas since these areas may also have high street runoff loads. The data is insufficient to arrive at a definite conclusion.

One study[27] was located which at least identified the types of metal responses expected for different metal-solid interactions. It was stated that, in general, processes depending solely on precipitation should yield a metal residual dependent only on the solubility product of the metal precipitate and complex formation (assuming that kinetic control can be ruled out). It was also correctly pointed out that, if suspended solids are not completely removed, then a portion of the metals associated with the fine particles will contribute to measured metal residuals even though the concentration in true solution is reflective of equilibrium conditions. If adsorption isotherms for various metals indicate that such a mechanism may dominate, then residuals should have a tendency to increase with an increase in influent metal concentration because of the asymptotic relationship between concentration and amount adsorbed. The actual mechanism probably contains elements of both models. In regards to increasing metal removal in a given unit process, the mechanism of removal is of secondary importance to the understanding of the process variables. However, to assess the partition of heavy metals between solid and solution phases, knowledge of the mechanistic aspects is essential.

The Metropolitan Sewer District of Greater Cincinnati performed a limited study in 1974, monitoring the influent concentrations of heavy metals to four plants in the District[28]. These data seem to group naturally into two sets. The median concentrations for Cr, Zn, Cu and Ni from the Mill Creek and Little Miami Plants are very comparable and exceed the median concentrations at the Sycamore and Muddy Creek Plants by factors ranging from two to six, depending on the metal. The reasonable conclusion is that the former two plants have a higher percentage of industrial dischargers. Sewer district personnel confirmed that this was indeed the case with the Little Miami and Mill Creek Plants having a large number of metal platers within their service areas. The Muddy Creek Facility was thought to be affected only marginally by industrial discharges and the Sycamore STP influenced not at all in this regard.

One other point concerning these data is of interest. At the Mill Creek Plant, which serves an area sewered by a combined system, rainfall was noted on Friday and Saturday, September 27 and 28. A total of 0.92 inch was recorded at the Cincinnati Observatory. Average daily flows (ADF) on these days were 107 and 130 mgd, respectively. The following week was dry and influent concentrations of the aforementioned metals on Friday of that week were higher for Cr, Zn, and Ni and only slightly lower for Cu. On Saturday, the concentrations of all four metals were far lower than they had been the previous week or even the previous day. On these days, 117 and 107 million gallons of wastewater were treated. Although it is difficult to statistically justify judgements based on such a small sample, the trend appears to support the hypothesis of Friday discharging by industries and also shows that urban runoff is perhaps of significance in increasing concentrations above base levels.

THE ULTIMATE FATE OF HEAVY METALS IN SLUDGES USED AS SOIL CONDITIONERS

The problem of the ultimate fate of heavy trace metals in sludge used as a soil conditioner has two distinct parts. On the one hand, there is the question of the phytotoxicity due to increased metal content of the sludge amended soils; on the other hand there is the question of the effect of changes in plant composition upon the animals consuming the plants.

Toxicity of Heavy Metals to Humans

A discussion of human metal toxicity due to plant uptake from sludge reduces to a discussion of cadmium. The toxic metals mercury and lead found in sludge do not show up in toxic concentration in the consumable parts of plants.[29] Other elements known to build up toxic concentrations in plants, as, for instance, selenium, are not usually found in sewage sludge. In corn grown under normal conditions it has been shown that these heavy trace metals which do appear in the grain are concentrated in the germ of the grain.[30] For instance, essentially all the Zn and approximately 70% of the Cd appear in the germ which represents 12% of the whole grain. Since the germ of corn which is used in processed foods is separated from the remainder of the grain (part to be pressed for oil and the remainder used as cattle feed), the possibility of the careful use of grain with an excess heavy metal concentration exists.

Cadmium is extremely toxic in humans; the normal human body burden is 15-30 mg for an adult, approximately half of which is in the liver and kidney.[4,31] A concentration of approximately 200 ppm in the kidney appears to be the threshhold level value for kidney dysfunction. Cadmium absorbed into the body has a residence time (half-life) of about 40 years. Attempts at mass balance calculations to determine a threshhold level of dietary intake to produce kidney dysfunction after 50 years of consumption are frustrated by uncertainties in the actual absorption rates of ingested Cd and the normal loadings of Cd in the body. The range of possibilities within the present state of our knowledge is between 100 and 1,000 μg/day.[4] This allows a safety factor in our current dietary dose rate of somewhere between unity and thirteen. It is fairly clear that the lower value is too small as it is close to the present average dietary intake and chronic Cd toxicity does not appear widespread. Nevertheless, the safety factor is small and unknown so that any additional input of Cd into the human diet should be viewed with concern.

Cadmium uptake by plants from sludges applied to the soil is a very complicated phenomenon. As a generality, the only statement that can be safely made is that increasing the soil Cd content will effect a change in plant Cd in the year the sludge is applied. Furthermore, the relationship is linear with the added soil Cd[32,33] to well beyond the point at which Cd toxicity causes major reductions in the yield from the plants. The slope of this curve depends on a number of factors, including but not necessarily restricted to:[29]

- Soil pH
- Plant species (and variety)
- Plant part considered
- Temperature

For instance, lettuce which picks up about 10% of the added Cd in slightly acid, sandy soil, and chard accumulate more Cd than do peas. In peas the seed picks up a larger percentage than the foliage; in radishes, more Cd will be found in the leaves than in the root.

To date the review of the available literature shows insufficient information to make definitive statements about Cd concentrations in plants on sites on which municipal sludge has been spread for long periods of time. California experience[5] has involved the land application of sludges for over 30 years with no indication of Cd toxicity problems. These have, however, involved sludges from relatively primitive treatment methods; more advanced methods may deposit a larger fraction of the heavy metals in the sludge, so this situation may change. The Calumet Treatment Plant of the Chicago Metropolitan Sanitary District found[6] that in going to anaerobic digestion from lagoon settling, essentially all the Cd is retained in the sludge and the Zn carried away by the effluent is halved.

One of the longest experiences with landspreading is the land treatment system at Werribee, Victoria, Australia (treating Melbourne's waste) which has been in continuous operation since 1897.[40] This system has been a raw sewage treatment system but its experience with heavy metal should be indicative of the long term effects of spreading sludges on agricultural land. Unfortunately, only a very limited amount of data exists on the heavy metal loading in the influent. For instance, there is only one sample for which lead was measured and only three for cadmium; the latter measurements varied by more than a factor of ten so that it is difficult to determine which of these, if any, are representative. The other heavy metal data represents the June, 1968 through November, 1969 period only. Thus there is no long term data on heavy metal loadings.

With this important caveat in mind, the results of the Werribee experience indicates no increases of heavy metal loadings to toxic levels. All trace elements in the soil appear to have been increased (relative to an unirrigated control) as did the extractable amounts of these elements. These have increased in some cases to values outside the range of normal values for soils. In some areas the trace elements Zu, Cu, Cd, Cr, and Ni were noted in the forage grasses grown on the treated land although in no case was the increase to a level toxic to livestock; in some cases, a decrease (Cd in one 73-year old sample and Mn in each sample) was noted. The variation between samples grown on treated soil and those grown on the control is sufficiently large that no definitive statements can be made regarding the effect of long term treatment of land with sewage.

The results of the Werribee experience are ambiguous. On the one hand, no serious heavy metal problems have occurred as a result of more than 70 years of application of sewage to the soil. On the other hand, the available data is insufficient to tell us why no problems have arisen.

Most of the reports show increased Cd uptakes on soil treated with municipal sludge; exceptions include areas treated with low Cd sludge[29] and an Illinois study.[6] In the former study, grasses on the Hagerstown sludge farm which has received (low cadmium) sludge for 24 years show elevated Zn contents but Cd levels unchanged relative to control areas. In the latter study, the investigators found the trace metal uptake in corn and soybeans, to be a function of the total metal deposited during the current growing season and independent of the total deposited metal from earlier growing seasons. This has been observed by others and appears to indicate that annual loadings of Cd are more important than the total loading over a number of years.

Studies with chard[34] indicate that plants grown on soil treated with composted sludge show less Cd uptake than those treated with fresh sludge. It isn't clear exactly what aspect of the composting operation is responsible for the difference in Cd uptake but the composted sludge has a much higher pH than uncomposted; low pH tends to increase plant uptake of Cd. There is also the possibility that, in composting the organic matter chelates heavy metals[29], thereby making them unavailable to plants. Other observers[35] have noted, however, that metal availability is more complicated than a simple question of water solubility. It has also been observed that direct application of the heavy metals without the accompanying organic matter characteristic of sludges leads to higher immediate plant reactions.[35] There is no evidence as to the mechanism which prevents or delays the plant reaction to the heavy metal nor any indication as to the persistence of this protective mechanism over a period of time after the application of the sludges.

Toxicity to the Plant

Sludge amended soil need not be used to raise crops for human consumption (nor for consumption by livestock); a disposal farm might, for instance, be dedicated to growing Christmas trees or hybrid poplars for pulpwood. In such a case, the toxic reaction of the plant to the heavy metals in the sludge is more important than the uptake of metals toxic to humans.

The question of plant toxicity to heavy metals is very similar to that of plant uptake. The metals involved in sludge are most likely Zn, Cu, and Ni; Pb could be toxic but the PO_4 in the sludge apparently acts to make the Pb unavailable. Phosphate is thus a helpful component of the sludge as it also helps to make Zn unavailable;[(29)] however, in some cases, phasphate concentrations and phosphate toxicity may be the limiting factor in sludge application rates.

The factors relating to sludge toxicity are basically the same as those for plant uptake except for the variation of the toxic effect with metal. In general, lowering the pH increase, the availability, as does a high C.E.C. Individual crops will vary considerably in their ability to tolerate heavy meatls as will varieties within species.

Sludge Treatment of Surface Mine Spoil Banks

The application of sewage sludge to surface-mined areas produces beneficial effects. In most cases, even if attempts at reclamation have been made, the topsoil has been lost or mixed with other overburden in the strip mining operation. The surface soil then is typically sufficiently low in pH and high in toxic metals that few vegetative species can grow on it. Treating this soil with municipal sludge improves growing conditions in several ways. Typically the addition of sludge raises the pH of the soil, introduces organic matter, and introduces considerable quantities of phosphate;[(36)] each of these tends to make the existing metal concentration less available to the plant. In an experiment in which corn was grown on sludge amended strip mine soil, the heavy metal concentration of the corn was higher in the control than in the test plot[36] (This was ascribed in part at least to the growth under stress conditions as the control yield and quality were each very poor.) In other experiments with grasses and leaves, the metal concentrations varied from "normal to moderately high" and was very species dependent.[37,38]

From the literature reviewed, it is not possible to make many definitive statements about the long term effects of sludge application to cropland in terms of build up of toxic metals. Since the factors for Cd uptake are so many and the functional dependence so poorly known, an extremely conservative point of view would appear prudent for sludge spreading on land with crops intended for human consumption. Because of successful results in some experiments in this area (the Hagerstown experiments[29] and the Illinois work[6])more work must be done. In each of these experiments the metals have been applied to the soil. They have gone somewhere. If not into the plant--where? Have they in some way been made inaccessible to the plant while remaining in the soil or have they been carried off in surface water. A careful mass balance of applied metal, absorbed metal, and soil metal buildup must be made. If some mechanism has made these metals inaccessible to the plant, what is this mechanism and what are the limits on its operation? Can these crops safely be used for feed for livestock? These first-order questions need to be answered.

Second order questions which also should be considered include:

- What synergisms or antagonisms exist between the various trace metals?
- How do the heavy trace metals revert to forms inaccessible to plants? Can this process be stimulated artificially?

The application of sludge to surface mined land appears to be an attractive concept, since it can make unproductive land productive. Since the problem in this case can be pre-existing excess heavy metals concentrations careful monitoring of food stuffs grown on such soils would be needed. Consideration of dedicating such land to non-food crops might be given.

CONCLUSIONS

The foregoing analysis points out one fact clearly. Unless additional insight into the process of pickup of metals by waste-activated sludge is gained, little use can be made of the data base on metal content of sludges. Frequently, cities showing high influent concentrations achieve sufficiently poor removals that sludge concentrations of a given metal do not exceed statistical criteria of abnormality. In such cases effluent discharge criteria may be needed to protect downstream water quality. On the other hand, the concentration ratios of certain treatment plants may be high enough to cause concern over metal content of the sludge, even though inflow values may not indicate that a problem exists.

Attempts to fill in gaps in data by extrapolation can only yield approximations due to the complexity and nature of interactions between heavy metals and solid surfaces. Operating policies of individual STP's also cause difficulties in estimation because of recycling, poor sampling design, or contamination. The options might include a requirement to establish more precise mass balances of heavy metals in those areas where statistical criteria indicate a need. The calculation of the geometric mean of expected within-plant metal removal performance (as concentration ratios or fraction removed) may allow the use of previously collected information on metal concentrations in sludges; alterations in process variables or influent metal characteristics would necessitate a reevaluation of plant performance. High influent or sludge concentrations of certain heavy metals may very well point to an industrial discharger, but, lacking additional information, any conclusions must be qualified.

Although a number of studies were located which examined the effects of tertiary treatment (generally using lime or alum) on effluent trace heavy metal concentrations[22,27,39], little consideration has been given to the increased sludge metal loads or to the disposal of the increased volumes of sludge which will be generated.

In total, it appears that regulation of industrial dischargers will, in fact, produce reductions in the levels of heavy metals in both sludges and effluents. On the other hand, a blanket statement covering all industries known to utilize or discharge heavy metals would be very costly from the standpoint of enforcement as well as treatment.

Other alternatives are available. In some areas, sludges may have a low metals content even though some industrial loading occurs. Some means of distinguishing these situations is clearly necessary since it cannot be documented that improvements will result in every case when limits are set on industrial discharges.

Project Contacts

George Walkenshaw, Columbus, Ohio - Columbus monitors the influent to and effluent from the treatment facility and the effluent from all industries which have toxic or strong wastes. The purpose of this program is to establish appropriate surcharges for BOD, nitrogen, phosphorus, and suspended solids. At present there are no plans to include toxic materials in the surcharge scheme as there is no evidence that they increase treatment costs.

Robert Carter, Canton, Ohio - Canton monitors the metal content of the influent, effluent, and sludge produced at their STP. They find approximately 200 ppm Cd in their sludge but do not detect--by their measurement technique (AA)--Cd in the influent. They do have volumetric metering on most of the local industries and do take periodic samples of effluent for testing. These data they regard as proprietary to the industries in question but could be made available with the appropriate EPA groundwork. The utility of these data might be slightly questionable as among the industries which are currently not metered are Canton's two largest industries.

Stanley Whitebloom, Coordinator of Industrial Wastes, Chicago Metro Sanitary District - Chicago requires point source pretreatment for big platers. He felt platers were the main source of heavy metals, or rather, main controllable source. They have a great deal of data on this particular source. They have some sketchy information on runoff and influent to treatment facilities, but do not feel it is defensible in a mass balance. Chicago has more than 5500 miles of sewer to which the exact number of hookups is not known with any degree of accuracy. The Sanitary District staff believes other industrial sources and street runoff are probably significant in themselves, since tight regulation of platers has resulted in only moderate reductions in sludge metal content.

Several suggestions were made with regard to research needed prior to policy formulation:

(1) More information is needed on the relationship, if any, between metal concentrations in sludge and plant uptake/human health effects.

(2) Agreement should be reached between guidelines being promulgated by EPA and the Department of Agriculture, respectively.

(3) Mass balances should be required only in special cases since to perform an adequate study for a city like Chicago would be prohibitively expensive.

(4) If a single number is to be stated as a maximum sludge concentration or loading, then the reasoning behind the stated value should be published in detail so it can be supported by subsequent experimentation.

Dr. Cecil Lue-Hing, Director of Research, Chicago Metro Sanitary District - Didn't want to talk over the phone. Responded to our letter by sending us several publications of the district pertaining to the occurrence and behavior of heavy metals in their system and at their disposal site.

Ross Caballero, Los Angeles - We discussed the use of sludge as a soil conditioner in California; Kellogg's (dried sludge) has been used for 35-40 years with no ill effects. He did observe that, in the past, this sludge was derived from primary plants with 30-40 percent solids removal; new plants will remove ≈ 60 percent and expected technology will remove 70 percent. This change in process may effect major changes in sludge pick-up of toxic metals.

They recently started a project to measure plant pickups using wastewater for irrigation and sludge used as a soil conditioner. Unfortunately, the man who was the guiding spirit left and the project has only recently been reinitiated.

They have data from an upstream treatment facility (as LA is spread out, with residential areas in the hills, primary treatment facilities have been constructed partly for hydraulic relief). If the data from this facility which serves an upper class residential neighborhood are extrapolated to the city as a whole, they find:

	Residential Percentage	Nonresidential Percentage
Cd	17	83
Zn	25	75
Cu	13	87
Cr	2	98
Ni	12	88
Ag	45	55

The silver they interpreted as being an upper class artifact, the result of photography as a hobby.

They are going to try to get better data as this is necessary to establish a basis on which to charge for sewage services. They want to get a good cross-section of the community-industrial, commercial, and residential with the residential category subdivided according to socio-economic status. They are trying at the moment to find a method of automatic sample collection. At the early stage in the sewage system from which they wish to extract samples, the influent is insufficiently disaggregated to provide homogeneous samples. They hope to resolve this difficulty in the next few months.

Larry Klein, New York - He is a bit defensive about the article he and others published as reaction to it has not been uniformly favorable. He is very anxious for others to repeat the experiment and is eager for someone to examine his data and therefore the conclusions. The data collection is massive.

Dick Field, EPA, Edison, New Jersey - We contacted Mr. Field regarding data on runoff contributions to metal loading. He sent us a number of studies most of which measured total street loads. Some idea of the actual sewer loads could be obtained (see section on street runoff contributions).

Gr. Cincinnati Sewer District - Discussions with several District personnel to obtain operating information on treatment plants, mean daily flow, residential versus industrial nature of influents, and combined versus separate sewers.

Rufus L. Chaney (USDA) - He has done much work in the area of plant pickup of toxic metals. He referred us to several publications of his in this area which he sent to us. He did note that the question of livestock pickup was completely unexplored. He also observed that the plant pickup situation involves enough variables in a sufficiently complicated way that an investigator can get any answer he wants, e.g., choice of corn versus a leaf vegetable would lead to differing conclusions as to the potential dangers associated with plant pickup.

Ronald Cherry (Atlanta) - They have performed analyses on urban discharges from various areas near Atlanta. The data are obtained from receiving streams and there is apparently no way to correlate the weighted loading or concentration to a particular source.

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