Effect of Processing Mode on Trace Elements in Dewatered Sludge Products

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ABSTRACT

Minimization of the concentration and mobility of trace metals is a primary concern when considering the land application of wastewater sludges. The effects of pelletization/drying, composting, incineration, and N-Viro[TM] chemical stabilization on composition and mobility of trace metals and P were compared. A single day's production of dewatered anaerobically-digested sludge (Syracuse, NY) was used as the sole initial feedstock so that observed differences would solely be a result of the process used. Processes were carried out in full-scale municipal facilities with the exception of pilot-scale pelletization/drying. Total analysis was determined by inductively-coupled plasma (ICP) spectroscopy. Mobility was measured using the Toxicity Characteristic Leaching Procedure (TCLP).

Analyte concentrations were essentially constant during dewatered sludge production with mean values (mg kg^{-1} total solids) of 5.6 Cd, 10.7 Co, 130 Cr, 587 Cu, 49.7 Mo, 35.8 Ni, 26880 P, 132 Pb, and 545 Zn. Concentrations in dried pellets were similar to the dewatered sludge, but were reduced in composted sludge due to the addition of wood chips. Only Mo exceeded USEPA §503 exceptional quality (EQ) limits in these three products. Concentrations were reduced by dilution in the N-Viro product so that it met all EQ limits. Incineration concentrated all analytes except for Cd and Pb, which experienced volatilization losses.

The TCLP-mobile fraction (percent of total) of all analytes in dewatered sludge was below 3% except for Ni (7.1%), P (6.0%), and Zn (11.2%). Composting slightly increased Cd mobility, but reduced that of Ni and P. Pelletization increased the mobility of Cd (7.9%), Cu (3.8%), Ni (15.4%), and Zn (15%). The N-Viro process substantially increased mobilities of Cu (43%), Mo (50%), and Ni (24%) at elevated pH. Incineration slightly increased mobilities of Cd and Mo, but reduced Ni, P and Zn mobility. While changes in total concentration from the dewatered sludge feedstock followed a predictable pattern, the mode of processing had widely ranging effects on mobilities, from total immobilization on one hand to substantial mobilization on the other. These results, in combination with those of longer term *in situ* studies, can be used to guide the selection of sludge processes to result in the minimization of potential metal and P mobility.

ADDITIONAL KEY WORDS

Sludge, biosolids, composting, pelletization, incineration, N-Viro, TCLP, heavy metals, mobility, extraction

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INTRODUCTION

With increasing landfill costs and the loss of ocean dumping as an alternative, land application has become an increasingly attractive sludge management option to municipalities seeking to minimize the costs and environmental impacts of sludge management, especially when the potential benefits of conserved nutrients and organic matter are considered. Perhaps the primary concern associated with land application of sludge is the mobility and availability of trace metals and (more recently) phosphorus. A variety of sludge stabilization processes are available, including composting, pelletization and drying, chemical stabilization, and incineration. One would anticipate that these diverse processes would have widely ranging effects on trace metal and nutrient mobilities, the most desirable being immobilization of trace metals.

Extractability or leachability is commonly used as an empirical index of short-term mobility of trace metals in sludge and sludge products. The results of a variety of single or sequential extractions have been reported (Table 1) for a range of sludges (Lake *et al.,* 1984) and sludge products. Lagerwerff *et al.* (1976) measured water leachability of dewatered sludges from Baltimore, MD and Washington, DC. Petruzzelli *et al.* (1994) used sequential extractions to characterize metal mobility. Mohamed *et al.* (1991) determined the extractability of dewatered sludge and subsequent incinerated sludge ash using the California Waste Extraction Test (WET). Fraser and Lum (1983) used sequential extractions to determine mobility of metals in incinerated sludge ash.

Frink and Sawhney (1994) measured TCLP extractability of Cd, Cr and Pb of composted sludge from Hartford, CT. Trace metal mobility in a sludge/municipal solid waste (MSW) co-compost was determined via water extractability by Sims and Kline (1991). Other composting data (Tisdell and Breslin 1995, Leita and De Nobili 1991) focuses on MSW-derived composts. Extracted metal concentrations were measured by Bennett *et al.*, (1989; also cited in Burnham *et al.* 1992) for chemically-stabilized (N-Viro™ process) using a modified USEPA Extraction Procedure (EP) test. Studies measuring the extractability of dried or pelletized sludge were not found.

The objective of this study was to determine the effect of sludge processing (pelletization/drying, composting, incineration, and N-Viro chemical stabilization) on the concentrations and mobilities of trace metals and phosphorus. Because sludges originating from various municipalities have differing metal compositions and speciations (Ravishankar *et al.,* 1994), a homogenous digested dewatered sludge feedstock from a single source was used to ensure that the resulting product composition and metal mobilities would be solely a function of the mode of processing. The TCLP method (Method 1311, USEPA 1992), a standardized weak acetic acid extraction for assessing mobility of a variety of analytes from materials, was selected to characterize mobilities of trace metals and phosphorus. The sludge products generated in this study are also being used in a larger project determining the effects of both the sludge processing mode and the physical and chemical characteristics of the receiving soil on long-term trace metal mobility.

METHODS

Facility information

The sludge products were derived from dewatered digested sludge produced on May 16, 1994 at the Onondaga County Drainage and Sanitation Department's wastewater treatment facility in Syracuse, New York. Primary and secondary sludge produced at the plant is anaerobically digested and subsequently dewatered in a belt press to approximately 220 g /kg⁻¹ (22%) total solids (TS). Nearly the entire day's production on May 16 was used for this experiment.

In order to verify the consistency of metal concentrations in the dewatered sludge, grab samples were collected from the belt press conveyors at 30-min intervals from 00:00 (midnight) to 21:00 hours. From 00:00 until 13:45 the sludge was loaded on three roll-off bed trucks (total wet weight of 52,000 kg) for transport to the incineration facility near Rochester, NY, and between the second and third roll-off trucks, on a truck for transport to the composting facility in Lockport, NY (wet weight 30,000 kg). This process was interrupted at 12:00 for filling six plastic-lined drums with dewatered sludge (which served as a sample of the initial feedstock) for shipment to Cornell University, followed by seven drums for pelletizing/drying at Clarkson University in Potsdam, NY. The balance of the day's sludge production was fed through to the on-site N-Viro stabilization facility.

Sludge incineration was carried out in a multiple hearth furnace at Monroe County's Northwest Quadrant facility in Rochester, NY. Continuous incineration began at 09:30 on May 16, with the last of the sludge fed into the incinerator at 00:30 on the 17th. Plant operators estimated that approximately 6 h were required to purge out any residual local sludge ash from the furnace. By 18:30 on the 16th the peak process temperature reached 790°C, further increasing to 815°C at 22:30. Drums for

shipment to Cornell University were filled near the end of the run.

Pelletization was carried out in a California Pellet Mill Series C pilot-scale pelletizer at Clarkson University, set to produce pellet diameters of 6.5 to 7 mm. A conveyor transferred the pellets to a Middleby Marshall rotating grate oven, which was used to dry the pellets to a final solids content of approximately 950 g kg^{-1} (95%) TS. Two sealed drums of dried pellets were shipped to Cornell University.

Composting was carried out at the municipal sludge composting facility in the City of Lockport, NY. Sludge was mixed on May 16 with new wood chips (from chipped shipping pallets) at an initial sludge/wood dry weight ratio of 0.91, resulting in an initial mixture solids content of 450 g kg^{-1} (45%) TS. (The wood chips contained no detectable trace metals except for 7.8 mg kg^{-1} Zn.) Windrow dimensions were 5.2 m wide by 5.5 m long; the material was isolated from local compost by wood chip buffers on either end of the windrow. Cured compost was sampled on Aug. 2, with a final solids content of 790 g kg^{-1} (79%) TS. Normal on-site screening and recycling of large wood chips was not carried out. Instead, six drums of the final composted mixture were shipped to Cornell University, where the on-site screening of chips was simulated using a sieve (4.7 mm openings, approximately equivalent in size to the on-site screening equipment). Screening resulted in retention of 42.4% of the dry solids on the sieve. The retained wood chips were completely coated with sludge material. The composted sludge that passed through the sieve still had a substantial fine wood chips content, and was scanned with a strong magnet to remove any metallic particles originating from nails in the wood pallets.

Chemical stabilization via the N-Viro™ process (Burnham *et al.,* 1992) was carried out on-site at the sewage treatment plant. The dewatered sludge was transported by conveyor from the belt press to a pug mill, where it was mixed with lime kiln dust (primarily CaO) and cement kiln dust at nominal addition ratios of 15 and 42% of sludge wet weight, respectively. In the N-Viro process, the combined effects of exothermic heating, high pH (12.3-12.4), ammonia release and low moisture content stabilize and pasteurize the mix. The product was allowed to cure (minimum of 4 days, turned twice daily) in windrows, isolated from other days' material. The final solids content measured on-site was 630 g kg^{-1} (63%) TS. The only trace metal concentrations in the alkaline amendments comparable to levels in the dewatered sludge were 13 mg kg^{-1} Co and 25 mg kg^{-1} Ni in the lime kiln dust.

Sample handling and analysis

All products were shipped and stored in plastic-lined sealed drums. Upon arrival at Cornell University, the dewatered sludge, composted sludge, and pelletized sludge were refrigerated at 2 to 5°C, while the incinerator ash and N-Viro products were stored at room temperature. Hand-milling (using a porcelain mortar and pestle) was required to break up large particles in subsamples of N-Viro and ash to achieve suitable homogenization prior to analysis.

Samples for total elemental analysis were dried at 55°C and finely ground with a mortar and pestle. Perchloric acid (wet) digestion was used to prepare the samples for inductively-coupled plasma (ICP) spectroscopic analysis at Cornell University's Nutrient Analysis Laboratory, using a Thermo Jarrell-Ash Model 975 ICP system. Four replicates were analyzed for dewatered sludge, N-Viro, and incinerated ash, while composted sludge and pellets were analyzed in triplicate. For Cd and Co, dry ash preparation was required (in triplicate for all sludge products), in which samples were ashed at 450°C overnight and, after cooling, treated with 30% H$_2$O$_2$. The samples were again ashed for 2 h and then dissolved in 12 M HCl prior to ICP analysis. For reasons of economy and timeliness, the time-series dewatered sludge samples used to monitor sludge uniformity were analyzed only by dry ash preparation, which, as is typically the case, resulted in lower recoveries for most analytes. Solids analysis was carried out by standard gravimetry.

For TCLP extractions, a mass of each sludge product containing 5 g TS was weighed into a 125-mL HDPE bottle, to which was added 100 mL of TCLP extraction solution #2 (0.092 M glacial acetic acid, pH 2.91) in order to achieve the prescribed 20:1 extractant/TS ratio. An initial screening showed that the less acidic extraction solution #1 (0.092 M glacial acetic acid plus 0.064 M NaOH, pH 4.93) was not suitable. It should be noted that no size reduction of pellets was carried out, because the prescribed narrowest dimension limit of 1 cm was not exceeded. It was subsequently observed that a portion of the pellets retained their overall shape during the period of mixing, thus potentially limiting the degree of extraction. (Similar durability of pellet structure in soil has since been observed in our greenhouse application experiments.) Both N-Viro and dewatered sludge sample bottles were briefly vented after several minutes of mixing in order to allow excess gas (CO$_2$ generated by carbonate reaction with the

extraction solution) to escape to prevent subsequent leakage.

Extraction was carried out for 19.5 hours (within the prescribed window of 18 ± 2 hours) at room temperature (22°C) using a TCLP apparatus that provided end-over-end mixing at 30 rpm. A portion of the liquid fraction was decanted from each bottle, briefly centrifuged at moderate speed (1400 g), and filtered through a 0.8-μ TCLP glass fiber filter (Micro Filtration Systems GF75). Filters were acid washed and rinsed with distilled/deionized water prior to use. Liquid remaining in the extraction bottles was tested to determine final extraction pH. Filtered samples and solution blanks were then immediately submitted for ICP analysis. Results are based on triplicate TCLP extractions, one of which was reanalyzed, yielding a total of four ICP analyses ($n=4$). For Zn, one set of extractions had erratic results (exceeding total Zn) and was therefore discarded, resulting in $n=2$.

The significance of differences in total and TCLP-extractable analyte concentrations was tested at the 95% confidence level with the ANOVA/Duncan test, as implemented in the WinSTAR statistical program (Anderson-Bell Corporation, Arvada, CO).

RESULTS
Time series results

The concentrations of metals in the dewatered sludge were fairly consistent during the production run (Cu, Zn, Pb, Ni and Co shown in Figure 1). As expected, dry ash analyte recoveries were relatively low in comparison to wet digestion results reported below. Mean dry ash results (expressed as mean $\pm$ standard deviation, mg kg^{-1}) for several metals were: 556 ± 14 Cu, 31.8 ± 1.3 Ni, 493 ± 11 Zn, and 119 ± 4 Pb. As can be seen in the figure, Cu, Zn and Ni variability was greatest during the 00:00 to 02:00 filling of the first truckload for incineration, and again after 13:30, when transfer to the on-site N-Viro facility took place. Excluding these two periods from the calculations reduced the standard deviations but did not significantly affect the mean values: 559 ± 7 mg kg^{-1} Cu, 31.7 ± 0.9 Ni, 493 ± 7 Zn, and 120 ± 3 Pb. Total solids contents over the entire time period were consistent, with a mean value of 219 ± 70 g kg^{-1} ($21.9 \pm 0.7\%$) TS.

Elemental composition of the sludge products

Metal concentrations in the initial dewatered sludge (Table 2) were less than USEPA §503 exceptional quality (EQ) land application limits (USEPA, 1993) for all analytes except Mo. Molybdenum exceeded the EQ

limit but not the maximum ceiling concentration of 75 mg kg^{-1}. The composted sludge still had a significant fine wood particle content after screening, as reflected by the elevated volatile solids (VS) content. Concentrations of trace elements in the composted sludge were thus less than in the initial dewatered sludge, although Mo still exceeded the EQ limit. Reductions in concentrations were significant for Cd, Co, Cu, Mo, P, and Pb. The substantial dilution of the dewatered sludge solids with lime and cement kiln dust amendments in the N-Viro product was reflected in the reduced VS content. Because of this dilution, N-Viro trace element concentrations were significantly reduced, and all were less than EQ limits. Reliable ICP analysis of Pb was not possible because of spectral interference resulting from the large Ca content. The concentrations of most trace elements in the dried pellets were slightly elevated (although not significantly) relative to the dewatered sludge. This was most likely the result of slight variations in the initial dewatered sludge metals concentrations, since the similarities in VS content indicates only slight losses of volatile organics during the pelletizing and drying process. As with dewatered sludge, concentrations were less than EQ limits for all analytes except Mo.

Most trace elements were concentrated in the incinerated sludge ash because of the loss of VS during incineration, although the degree of enhancement was not uniform due to varying degrees of volatilization loss of the individual metals. (Incineration temperatures were well below the threshold level of approximately 875°C, above which heavy metal losses are nearly complete (Brunner, 1980).) Losses were greatest for Cd, which is volatile at incineration temperatures (metallic Cd boils at 765°C). For Pb, losses nearly offset concentration effects. Interestingly, all analytes remained within EQ limits except for Mo, which exceeded the maximum ceiling limit of 75 mg kg^{-1}.

TCLP Extraction Results

The pH values of the final extraction mixtures ranged from 4.6 to 4.8 for pellets, compost and ash (Table 3). The dewatered sludge final mixture pH was slightly higher at 5.6. The alkalinity of the N-Viro neutralized the weak acid extractant, resulting in a final mixture pH approaching 12.

The fraction of analytes extracted by the TCLP method was expressed both as the mass extracted per unit dry weight (mg kg^{-1}, Table 3) and as percent of the total analyte concentrations (Table 4). Cadmium was immobile in dewatered sludge, but was somewhat

mobilized in pellets (0.5 mg kg^{-1}, 7.9% of total). The remaining products had extractable Cd of 0.11 to 0.16 mg kg^{-1} (4 to 7% of total). Cobalt was also immobile in dewatered sludge and ash; observed mobilities for other products were not significantly greater, except for N-Viro (0.58 mg kg^{-1}, 11% of total). Chromium mobility (1.85 mg kg^{-1} in dewatered sludge, 1.4% of total) was reduced slightly in compost, N-Viro and ash, although it increased slightly in N-Viro on a percent-of-total basis.

Copper, barely mobile in dewatered sludge (0.98 mg kg^{-1}, 0.2% of total), was substantially mobilized by all processes. Mobility was greatest in N-Viro (51 mg kg^{-1}, 42.9% of total), likely resulting from the dissolution of organic matter (and hence organic-Cu complexes) at elevated pH. Pellets (23 mg kg^{-1}, 3.8% of total) and ash (21.5 mg kg^{-1}, 1.8% of total) had similar Cu mobilities. Molybdenum followed a similar pattern, with mobility greatest in N-Viro (4.9 mg kg^{-1}, 50% of total), followed by ash (4.5 mg kg^{-1}, 4.8%) and pellets (1.5mg kg^{-1}, 2.7%).

The mobility of Ni in dewatered sludge (2.5 mg kg^{-1}, 7.1% of total) was doubled in the pellets, and was substantially larger on a percentage basis in N-Viro (3.1 mg kg^{-1}, 24.2% of total). This, again, was possibly the result of organic matter dissolution, because Ni, like Cu, has an affinity for organic complexation. Lead (0.8 mg kg^{-1} in dewatered sludge, 0.6% of total) was rendered even less mobile in compost, pellets, and ash. The dewatered sludge mobile Zn fraction (60.9 mg kg^{-1}, 11.2% of total) was increased in pellets (84.7 mg kg^{-1}, 15%), reduced in ash (39.1 mg kg^{-1},4.1%), was relatively unaffected in compost, and was immobile in N-Viro.

Phosphorus extractability was greatest in the dewatered sludge at 1606 mg kg^{-1} (6% of total), followed by compost at 497 mg kg^{-1} (2.4% of total). The reduced mobility in compost was expected, because of dilution of the initial sludge by added wood chips. However, reduced mobility in pellets (241 mg kg^{-1}) was surprising, perhaps attributable to complexation/precipitation under the elevated processing temperatures. The low P mobility in N-Viro was likely due to precipitation reactions favored at elevated pH and Ca levels.

DISCUSSION

The observed consistency in the dewatered sludge time series demonstrated that the initial feedstock for the various processes was sufficiently homogenous for meaningful comparison of processing effects. The coefficients of variation (standard deviation as a percent of mean value) for the period 02:00 to 13:30, during which sludge for incineration, composting, pellets, and dewatered sludge storage was produced, were consistently low: 1.3% for Cu and Zn, 2.7 to 2.9% for Mo, Ni, and Pb, and 5% for Cr and P. The sludge generated during the first period of slightly greater variability (00:00 to 02:00) was loaded in the first incineration truckload, which was used only for initial purging of the incinerator. The second period of greater variation (after 13:30) was during transfer to the N-Viro process, which tended to homogenize the incoming sludge during accumulation and mixing in the mill. Overall, mean values for the time series were unaffected by inclusion of the periods of greater variation. Furthermore, any slight variations in initial concentrations are canceled out when mobilities are expressed as a percent of total concentration.

The dewatered sludge and resulting products generated in this study compared favorably with USEPA §503 standards. The dewatered sludge, compost and pellets satisfied all EQ limits except for Mo. The N-Viro product satisfied all EQ limits, and only Mo in the incinerated sludge ash (a product that would not be considered a candidate for land application) exceeded the maximum limit for land application. Changes in total trace metal composition from the initial dewatered sludge to the various products followed the pattern that one would intuitively anticipate: no change for pellets; reductions due to amendment dilution for composted sludge and N-Viro; and, for ash, concentration of most analytes, offset to varying degrees by volatilization losses.

TCLP, like other extraction protocols, is used as an empirical index of short-term mobility. In view of the wide range of initial sludge compositions, metal speciations, sample handling procedures and extractants used, it is not surprising that meaningful comparison of our data with other reported mobility data is difficult, even when results are expressed as percent of total composition (Tables 1 and 4). For example, Zn, with a TCLP-mobile fraction of 11.2%, was the most mobile analyte in the present study's dewatered sludge. In contrast, Lagerwerff *et al.*(1976) measured water extractabilities of 0.2% (Washington sludge) and 35.2% (Baltimore sludge), while the water and KNO$_3$ mobilities measured by Petruzzelli *et al.* (1994) were all less than 3%.

For other metals, Lagerwerff *et al.* (1976) found comparable Cu and Pb mobilities, but much larger Cd concentrations than reported here. Petruzzelli *et al.* (1994) observed Cd, Pb, and Cr mobilities that were

comparable to this study, but Cu and Ni mobilities were substantially greater; Cd mobility increased substantially and Pb increased slightly when a second KNO_3 extraction step was added. The WET extraction (0.2 M sodium citrate, pH 5) used by Mohamed *et al.* (1991) resulted in greater mobilities for Cd, Pb, Zn, and a much greater Cr (50% of total) than in the present study. Only Cu extractability was equal.

Frink and Sawhney (1994) measured composted sludge TCLP extractabilities similar to the present study. Assuming the standard 20:1 TCLP extraction ratio, their extractabilities (expressed as percent of total content) were <4% Cd, 1.1% Cr, and 1.2% Pb. Sims and Kline (1991) reported water-extractable mobilities of Cd, Cr, Cu, and Pb in a co-composted sludge/MSW that were comparable to the composted sludge in the present study, but Zn mobility (3.9%) was substantially less, and Ni (28.6%) was much greater. Substantial reductions in trace metal mobilities observed during composting of MSW (Leita and De Nobili, 1991; Tisdell and Breslin, 1995, and others cited therein). In contrast, reductions in Ni and Pb mobilities resulting from composting in the present study were only moderate; Cr, Mo and Zn remained relatively constant, and Cd and Cu mobilities increased.

It was estimated from the composition of the dewatered sludges and alkaline amendments (using nominal addition ratios) that the percentages of trace metals in the N-Viro originating from the dewatered sludge feedstock were: 98% of P, 94 to 95% Zn, 92 to 94% Cu, 81 to 84% Mo, 63 to 66% Cd, 60 to 61% Ni, 68 to 71% Cr, and 40 to 44% of Co. This demonstrated that the N-Viro's mobile Cu and Mo fractions originated primarily from the dewatered sludge. Conversely, it is numerically possible that the increases in mobility observed for Cd, Co, Cr, and/or Ni could have been attributable to mobility of these metals originating in the alkaline amendments. However, cement kiln dust mobilities measured by Bennett *et al.* (1989) using the USEPA EP extraction procedure at pH 11.5 were only 26% of total Cu, 22% of Ni, and 6.5% of Cr. Applying these fractional mobilities to the estimated amendment contributions would suggest that the majority of mobilized Ni in N-Viro was not directly a result of mobile Ni in the alkaline amendment, but more likely resulting from organic matter dissolution, as suggested previously.

The somewhat striking mobilities of Cu, Ni, and Mo in N-Viro reported here were substantially greater than N-Viro mobilities reported elsewhere. Bennett *et al.* (1989) assumed (correctly, in terms of free metal ion

chemistry) that acidic pH conditions would maximize metal mobilities. Accordingly, they modified the USEPA EP procedure (predecessor to the TCLP) to allow unlimited acetic acid additions during the first hour of mixing in order to force various final extraction pH levels of 5 to 8. Their assumption, however, ignored potential mobility at high pH levels resulting from dissolution of organic matter, and hence, organic-metals complexes. Thus, while their data demonstrated that the N-Viro's alkalinity often protected against mobilization at moderate to low pH (also Burnham *et al.,* 1992; Logan, 1990), the potential for substantial mobilization of complexed Cu and possibly Ni was not addressed, because no extractions were reported for the "native" pH of the N-Viro/extractant mixture, as was done in this study. (Further comparison with results in Bennett *et al.* was hampered by the fact that neither initial sludge composition nor dry weight extraction ratios were specified.) Although the mobility observed in this study may be deemed an unlikely *in situ* hazard at typical agronomic land application rates, it is a factor that bears consideration when the material is stockpiled or applied at extremely heavy rates.

Pelletization and drying in the current study significantly increased the mobility of all analytes except for Co and Cr, which were unchanged, and P and Pb, which were reduced. Other studies measuring the extractability of dried or pelletized sludge were not found.

WET procedure mobilities for incinerated sludge ash (Mohamed *et al.*, 1991) were all greater than the present study for Cd, Cr, Cu, and Zn by factors of 3 to 4, and for Pb by a factor of 60. Reported incineration temperatures were 815 to 870°C, slightly greater than the present study. Sequential extractions by Fraser and Lum (1983), who reported a wide incineration process temperature range of 760 to 960°C, resulted in little or no extractable metals with 1 M $MgCl_2$ or pH 5 sodium acetate/acetic acid extractants. When 0.04 M hydroxy-lamine HCl/25% acetic acid was used (much stronger than the TCLP extractant), Co, Ni, and Pb mobilities were 1.2 to 1.9%, only slightly greater than in the present study, although total concentrations in the ash were 14 to 15 times greater. Zinc mobilities were comparable, and Cd was less mobile. Phosphorus was immobile with the first two extractants, but was five times more mobile with the third extractant than the present study.

In summary, this is the only study of which we are aware that compares the effects of a range of full- and pilot-scale sludge processes on the composition and

mobilities of trace elements and P. Changes in total composition from the dewatered sludge feedstock followed a predictable pattern: reduced concentrations resulting from amendment dilution in composted sludge and N-Viro, concentration of most analytes in ash, offset to varying degrees by volatilization losses, and no change for pelletized/dried sludge. In contrast, the mode of sludge processing had widely ranging effects on individual trace metal TCLP mobilities, from total immobilization on one hand to substantial mobilization of initially immobile metals on the other. Understanding these effects may, in specific situations, contribute to the selection of treatment processes that reduce the mobility of elements of concern, in order to minimize potential environmental impacts of land application. It is not, however, realistic to directly extrapolate the observed TCLP mobilities to predictions of long-term *in situ* behavior in soil. Land-applied sludge products are subjected to a variety of additional factors that affect mobility of metals and P, including the degree of mixing with soil, soil pH and texture, the intensity of percolation, and the extent of preferential flow (Camobreco *et al.,* 1996). Ongoing work at Cornell University is extending this work by testing the short- and long-term *in situ* mobilities of these products (as reflected by leaching losses and plant uptake) when applied to undisturbed soil columns.

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Table 1. Summary of reported sludge extractability results. Extracted fraction expressed as percent of total trace metal content.

Study	Sludge Source	Extraction Method	Cd	Co	Cr	Cu	Ni	P	Pb	Zn
Dewatered sludge						*- mobile fraction as percent of total content -*				
Lagerwerff et al. (1976)	Washington, DC	water	4.6	-	-	0.4	-	-	0.3	0.2
	Baltimore, MD	water	11.4	-	-	1.8	-	-	0.2	35.7
Petruzzelli et al. (1994)	Italy (treated with Al polyCl)	water	0	-	0.5	5.7	16.4	-	0	2.0
		+KNO$_3$	8.0	-	2.3	8.2	38.0	-	1.3	2.7
	(treated with FeCl$_3$/CaO)	water	0	-	0.3	30.6	16.4	-	0	0
		+KNO$_3$	11.3	-	2.4	42.1	24.3	-	1.3	0.1
Mohamed et al. (1991)	Los Angeles, CA	WET test	3.3	-	50.4	0.2	-	-	7.3	19.2
Composted sludge										
Frink and Sawhney, (1994)	Hartford, CT	TCLP	<4	-	1.1	-	-	-	1.2	-
Sims and Kline (1991)	Wilmington, DE sludge/MSW	water	2.5	-	1.0	4.9	28.6	-	0.5	3.9
Incinerated sludge ash										
Mohamed et al. (1991)	Los Angeles, CA	WET test	14.9	-	1.4	8.5	-	-	6.6	12.2
Fraser and Lum (1983)	Hamilton, Ontario	MgCl$_2$	0	0	0	0	0	0	0	0
		+Na acetate	0	0	0	0	0.1	0	0.1	0
		+hydroxylamineHCl	1.0	1.9	0.1	0	1.9	2.6	1.2	3.6

Table 2. Sludge product composition: volatile solids (VS, as percent of total solids) and total ICP analysis results (mg kg^{-1} TS), mean and standard deviation. Values followed by similar letters are not significantly different (P=0.05). USEPA §503 exceptional quality and maximum ceiling limits (mg kg^{-1} TS) are included for comparison.

		Sludge Product Analysis						USEPA §503 Limits	
		Dewatered	Composted	N-Viro	Pellets		Ash	Exceptional Quality	Maximum Ceiling
VS, %	x	54.77	66.40	9.28	54.59		1.08	-	-
	sd	0.05	1.12	0.13	0.02		0.06		
Cd	x	5.62 a	4.21 b	1.58	6.43 a		3.58 b	39	85
	sd	0.25	0.80	0.10	0.44		0.48		
Co	x	10.70 c	8.47	5.18	10.42 c		23.10	-	-
	sd	0.08	0.45	0.07	0.53		0.65		
Cr	x	130 d	121 d	40	135 d		218	1,200	3,000
	sd	5	3	4	1		20		
Cu	x	587 e	469	119	606 e		1219	1,500	4,300
	sd	17	30	13	9		56		
Mo	x	49.7 f	32.7	9.8	55.3 f		95.1	18	75
	sd	5.3	3.3	5.3	2.8		8.9		
Ni	x	35.8 g	32.5 g	12.7	38.0 g		74.8	420	420
	sd	0.4	0.6	1.2	1.1		7.8		
P	x	26880 h	20630	4890	27700 h		71930	-	-
	sd	585	130	257	649		3175		
Pb	x	132 i	109	-†	137 ij		145 j	300	840
	sd	3	2	-†	2		6		
Zn	x	545 kl	458 k	115	567 l		959	2,800	7,500
	sd	30	23	4	25		81		

† - not available because of spectral interference; nd = not detected.

Table 3.		Sludge product TCLP extraction results: final extraction solution pH, and mean extracted trace metals and P (mg kg^{-1} TS), mean and standard deviation. Values followed by similar letters are not significantly different (P=0.05).							
		Sludge Product							
Element		Dewatered		Composted		N-Viro		Pellets	Ash
pH	x	5.62		4.62		11.96		4.81	4.69
	sd	0.10		0.02		0.01		0.08	0.04
Cd	x	nd	a	0.17	b	0.11	ab	0.51	0.15 b
	sd	-		0.08		0.08		0.10	0.08
Co	x	nd	c	0.02	c	0.58		0.22 c	nd c
	sd	-		0.04		0.36		0.14	-
Cr	x	1.85	d	1.35	de	0.97	e	1.92 d	1.18 e
	sd	0.41		0.22		0.39		0.19	0.29
Cu	x	0.98		9.75		51.0		23.0 f	21.5 f
	sd	0.58		0.82		5.0		1.7	1.8
Mo	x	0.56	g	0.55	g	4.93	h	1.50	4.52 h
	sd	0.18		0.17		0.42		0.12	0.16
Ni	x	2.54	ij	1.58	i	3.07	jk	5.84	3.66 k
	sd	0.14		0.46		0.62		0.40	0.87
P	x	1610		497	l	31		241 l	351 l
	sd	370		23		3.7		27	65
Pb	x	0.81	m	0.10	n	0.61	mn	0.08 n	0.08 n
	sd	0.49		0.17		0.47		0.14	0.05
Zn	x	60.9	o	52.5	o	nd		84.7	39.1
	sd	0.7		1.4		-		3.4	7.0

nd = not detected

Table 4.	TCLP-extractable trace metals as percent of total.				
	Sludge Product				
Element	Dewatered	Composted	N-Viro	Pellets	Ash
Cd	nd	3.9	6.8	7.9	4.1
Co	nd	0.3	11.2	2.1	0.0
Cr	1.4	1.1	2.4	1.4	0.5
Cu	0.2	2.1	42.9	3.8	1.8
Mo	1.1	1.7	50.3	2.7	4.8
Ni	7.1	4.9	24.2	15.4	4.9
P	6.0	2.4	0.6	0.9	0.5
Pb	0.6	0.1	-	0.1	0.1
Zn	11.2	11.5	nd	15.0	4.1

nd = not detected

Figure 1. Sludge production time series: Cu, Zn, Pb, Ni, and Co analysis (mg kg^{-1}, dry ash preparation) of 30-min grab samples of dewatered sludge, Onondaga County Treatment Plant, May 16, 1994.