Chemical Composition of Sewage Sludge from Selected Indiana Cities[1]

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Abstract

Sewage sludge samples were obtained from 10 Indiana cities and characterized chemically by determining the total amounts of 20 elements and the forms and amounts of nitrogen and phosphorus. The solids present in sewage sludge contained approximately equal amounts of organic and inorganic constituents with organic carbon values ranging from 15-28 per cent. The majority of nitrogen and phosphorus was present in inorganic forms. Fractionation of organic nitrogen indicated that amino acid nitrogen was the predominant form present. Heavy metal concentrations in sludge were highly variable; coefficients of variation ranged from 47 per cent for iron to 152 per cent for cadmium. In all cases, the bulk of heavy metals was associated with the sewage sludge solids. The results obtained suggest that chemical analysis of sewage sludge may be needed to prevent environmental pollution by sewage sludge disposal on agricultural land.

Introduction

Land disposal of sewage sludge is not a new concept but is one that is receiving renewed emphasis because of the costs involved in alternative disposal methods (*e.g.*, drying, lagooning, etc.). Furthermore, both cost and air pollution considerations have greatly hindered the wide-scale use of incineration as a disposal method (*cf.*, 8). However, before extensive systems involving disposal of sewage sludge on agricultural land are initiated, a thorough knowledge of the factors controlling the fate of sludge constituents in the soil is needed. A prerequisite to evaluating these factors is a quantitative assessment of the chemical composition of diverse sewage sludge samples.

The chemical composition of sewage sludge is dependent on the type of digestion and on the method of sludge handling employed during the sewage treatment process. In general, activated sludge contains 5-6% N whereas anaerobically digested sludge contains 2-3% N on a dry-weight basis (2, 13). Since essentially all K salts are water soluble, dewatering of sludge results in only trace concentrations of K (13). However, recent results indicate that 50-60 ppm soluble K and 1,600 to 1,800 ppm total K may be present in liquid-digested sludge (11). Since P compounds are sparingly soluble, the level of total P in sludge is relatively independent of handling procedures and averages from 0.1 to 1% on a dry-weight basis (2, 11, 13). Similarly, dried, dewatered, and liquid sludges generally contain comparable levels of heavy metals.

The concentrations of heavy metals (*e.g.*, Cu, Zn, Cd, Pb, Hg) in sewage sludge are receiving increased attention because of the possible

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effects of metals on plant growth and also because of the possible contamination of ground- and surface-waters with metals. With respect to plant growth, sewage sludge applications to soil may cause either metal toxicities (6, 13) or only excessive metal uptake and accumulation (12); however, the latter may be more important from a human and animal nutrition standpoint. A recent study indicated that soluble Cd concentrations in sludge-amended soils resulted in Cd toxicity in numerous crops (16). With respect to contamination of water resources, sewage sludge disposal on land may result in metals entering ground waters if the metal retention capacity of soil is exceeded. Obviously, the rates of sludge application on land must be consistent with prevention of crop toxicity and also contamination of water resources.

Before extensive studies are initiated to evaluate the disposal of sewage sludge on Indiana soils, data on the chemical properties of diverse sewage sludges are needed. Thus, the objectives of the study reported here are: 1) to determine the chemical composition of sewage sludge samples obtained from several Indiana cities, and 2) to evaluate the relationships between sewage sludge constituents.

Procedures

Bulk samples of anaerobically digested sewage sludge were obtained from the sewage treatment plant in the following Indiana cities: Anderson, Columbus, Crawfordsville, Greencastle, Kokomo, Lafayette, Lebanon, Noblesville, Peru and Tipton. In general, solids subjected to anaerobic digestion were derived from primary treatment. The wet sludge samples were stored in sealed glass containers at 4° C until subjected to chemical analysis.

The solids and ash content of sludge samples were determined gravimetrically by drying at 105° C for 16 hours and by igniting at 600° C for 3 hours, respectively. Total C was estimated by gravimetrically determining CO_2 liberated by H_2SO_4-H_3PO_4-$K_2Cr_2O_7$ digestion (1). Inorganic C was similarly determined after digestion with acid and $FeSO_4$ (1); organic C was obtained by difference. Total N was determined by a modified Kjeldahl procedure (15). Soluble + exchangeable NH_4^+ was estimated by steam distillation of MgO-KC1 amended samples followed by acidimetric titration of NH_3 (4). Organic N was fractionated by hydrolyzing samples with 6 N HCl and analyzing the hydrolyzate for total-, NH_4^+-, amino acid-, and hexosamine-N (5). Total P was estimated by HNO_3-$HC10_4$ digestion (17) and colorimetric determination of orthophosphate (14). A measure of total inorganic P in sludge samples was obtained by determining orthophosphate (14) extracted with 1N HCl; total inorganic P was extracted with 1N HCl to ensure recovery of both precipitated and sorbed inroganic P. Organic P was obtained by difference between total P and inorganic P values. Samples were analyzed for total K, Na, Ca, Mg, S (including SO_4), B, Fe, Al, Cu, Zn, Mn, Pb, Cr, Sr, Ba, Ni, As, and Hg by an independent laboratory.

The soluble concentrations of selected constituents in sludges were determined after removal of solids by either filtration or centrifugation.

Soluble inorganic P and Fe were determined by the colorimetric procedures of Murphy and Riley (14) and Jackson (9), respectively. Soluble NH_4^+ and NO_3^- were estimated by steam distillation procedures (4). Atomic absorption spectrophotometry was used for soluble Zn and Cd analyses.

Results and Discussion

The sewage sludge samples analyzed possessed a wide-range of per cent solids (Table 1). The per cent solids is a function of digester operation and no attempt was made in the present study to quantify the relationship between per cent solids and operation of the digestion units. Thus, to make valid comparisons of the total amounts of elements present in digested sludge samples varying in per cent solids, most data are presented as ppm in or as per cent of oven-dried solids. Furthermore, the results presented were based on batch samples taken from each treatment plant, recognizing that both temporal and vectoral variability exists within a given digester.

TABLE 1. *General characteristics of sewage sludges studied.*

Sludge	Per cent[1] Solids	Per cent of oven-dry solids[2]		
		Ash	Inorganic C	Organic C
Anderson	11.2	61	3	21
Columbus	5.7	50	1	27
Crawfordsville	1.5	48	1	27
Greencastle	2.3	47	1	28
Kokomo	9.9	52	2	27
Lafayette—2	19.7	69	2	20
Lebanon	6.9	49	2	26
Noblesville	0.6	50	1	24
Peru	0.7	60	1	15
Tipton	6.8	59	1	14

[1]Present in liquid sludge.
[2]Data obtained from analysis of wet sludge is expressed as a per cent of oven-dry solids.

Some general properties of the sewage sludges studied are presented in Table 1. The liquid samples contained from 0.6 to 20% solids with the majority of samples in the 1-10% solids range. A general discrimination between organic and inorganic constituents in sludge solids was obtained by determining the ash content of liquid sludge. In general, solids were composed of approximately equal amounts of inorganic and organic materials. Since salts soluble in the liquid portion of the sludge were not removed prior to ashing, the per cent ash in the solids obtained after filtration or centrifugation may be lower than the values reported, although the solid portion of sludge generally contains the bulk of the total concentration of many elements. Because weight lost on ignition generally overestimates organic matter in materials containing hydrous metal oxides or clay minerals, an independent method was employed for determining organic C. Based on oven-dry weight, the organic C content of sludges ranged from 15 to 28%. Inorganic C, most likely metal carbonates, comprised an insignificant percentage of the total C present in all sludges.

The forms of N in sewage sludge are shown in Table 2. The samples analyzed possessed a wide-range of total N contents (1.6 to 12.6%), with NH_4^+-N contributing from 16 to 60% (average = 33%) of the total N. The NH_4^+-N analysis performed measured both soluble and exchangeable NH_4^+-N. Separate soluble NH_4^+-N determinations indicated that only a small proportion of the total NH_4^+-N was present on the exchange complex of the sewage sludge solids (data not presented). As expected, the relative contribution of exchangeable NH_4^+-N was proportional to the per cent solids in the sewage sludge. The steam distillation procedure used for NH_4^+ analyses does not discriminate between volatile amines and NH_4^+ (7) and thus, the actual NH_4^+ levels may be lower than reported if the sewage sludge samples analyzed contained volatile amines. Analysis of NO_3^--N revealed that all samples contained < 2 ppm NO_3^--N, a reflection of the strictly anaerobic environment existing during sludge digestion.

TABLE 2. *Forms of nitrogen in sewage sludge.*

			Hydrolyzable N as % of total N				
Sludge	Total N (%)[1]	NH_4—N as % of total N	Total	NH_4	Organic	Amino acid	Hexosamine
Anderson	1.6	25	90	32	58	33	2
Columbus	4.7	45	81	46	35	24	2
Crawfordsville	7.2	40	95	51	44	25	2
Greencastle	5.6	34	94	44	50	32	1
Kokomo	1.7	17	94	21	73	41	2
Lafayette—2	2.1	22	80	30	50	31	1
Lebanon	2.8	20	90	25	65	45	3
Noblesville	12.6	60	87	65	22	15	2
Peru	8.0	51	83	57	26	14	2
Tipton	2.6	16	89	23	66	37	2

[1]Data obtained from analysis of wet sludge is expressed as a per cent of oven-dry solids.

The bulk of the total N in all sludges was solubilized during 6*N* HCl hydrolysis; recoveries ranged from 80-95% of the total N. Decomposition of some organic N (*e.g.*, amides) may occur during 6 N HCl hydrolysis. In general, 6 N HCl did not cause extensive organic N degradation since the change in NH_4^+ was in all cases < 10% of the total N (Table 2). The data indicate that amino acid-N accounted for ~ 50% of the hydrolyzable organic N. Since the procedure employed determined only α-amino N, it is likely that the percentage of amino acid-N was underestimated because several common amino acids contain more than one N atom per molecule (*e.g.*, lysine, arginine). The percentage of hexosamine-N was relatively low and never exceeded 10% of the hydrolyzable organic N. Relatedly, it has been shown that 6 N HCl hydrolysis will not recover hexosamine-N that is incorporated into polymers formed during oxidation of polyphenolic compounds (3).

Phorphorus present in sewage sludge was separated into three broad fractions: soluble inorganic, total inorganic, and total organic (Table 3). The total P content ranged from 1.2 to 4.5% and was composed primarily of insoluble, inorganic P. Even though soluble inorganic P values as high as 65.5 μg/ml were found, the bulk of the inorganic P was associated with the solid phase. As described in the procedures, an estimate of total inorganic P was obtained by determining the P extracted by 1 N HCl. This extractant was chosen to determine quantitatively the inorganic P that was present in the solid phase as a precipitate or as a sorption product. However, slight hydrolysis of organic P may have occurred during 1N HCl extraction, resulting in an overestimation of inorganic P. Since most naturally occurring organic P compounds are not hydrolyzed to a significant extent by 1N HCl, the values obtained should represent a reasonable estimate of total inorganic P in the sewage sludges analyzed. With the exception of the Greencastle sample, total inorganic P comprised > 60% of the total P.

TABLE 3. *Forms of phosphorus in sewage sludge.*

Sludge	Total P (%)[1]	Organic P as % of total P	Inorganic P as % of total P	
			Sorbed	Soluble
Anderson	1.41	34	65	1
Columbus	2.15	27	68	5
Crawfordsville	3.50	38	58	4
Greencastle	4.54	67	29	4
Kokomo	2.14	18	82	0
Lafayette—2	2.35	23	77	0
Lebanon	1.16	25	68	7
Peru	2.10	16	72	12
Tipton	2.46	12	87	1

[1]Data obtained from analysis of wet sludge is expressed as a per cent of oven-dry solids.

For both N and P, organic forms constitute a relatively low proportion of the total present indicating, as expected, that extensive mineralization of organic matter has occurred during digestion. In general, the organic C/N ratio of sludge (Tables 1, 2, 3) approximates that found in soil organic matter. Organic C/N ratios ranged from 3.9 to 17.9 and averaged 8.6. The organic C/P ratios, however, ranged from 21 to 92. It is likely that chemical rather than biological reactions control the accumulation of phosphate in sludge. Comparison of the C/N and C/P ratio observed in sewage sludge to the ratios found in readily decomposable plant residues indicates that neither N nor P should be a limiting factor in the decomposition of sewage sludge after incorporation into soil. Thus, the stability of the organic C will likely be the controlling factor in decomposition of sewage sludge after land disposal.

Results of elemental analysis of sewage sludge samples are presented in Table 4. The variability in chemical composition of sewage sludge samples is indicated by the coefficients of variation which range from 23% for S to 144% for Cd. Since the solid and liquid phases of sewage sludge samples were not separated prior to analysis, it can be anticipated that the bulk of some elements, *i.e.*, K and Na (as shown previously for NH_4^+), would have been present mainly in the liquid phase.

TABLE 4. *Elemental composition of sewage sludges.*

Element	ppm[1]		Coefficient of variation
	Range	Average	in %
Ca	52,500-154,500	79,200	38
Mg	6,500- 17,900	11,800	34
Na	1,100- 25,400	7,900	112
K	700- 14,900	4,300	105
S	6,400- 13,900	10,400	24
Fe	6,000- 36,200	20,900	47
Al	3,900- 18,600	9,200	64
Cu	300- 11,700	2,800	137
Zn	870- 28,400	8,100	117
Mn	200- 1,470	750	64
Pb	450- 1,900	770	56
Cr	50- 19,600	4,300	147
Ni	70- 3,500	1,000	132
Ba	100- 3,000	1,000	79
Sr	120- 650	280	57
Cd	3- 810	170	152
Hg	1- 13	4	94
As	5- 30	10	73
B	5- 79	23	108

[1]Data obtained from analysis of wet sludge is expressed as ppm in oven-dry solids.

Heavy metals in sludge were not soluble, but were associated with the solid phase (Table 5). These results are in agreement with previous studies (11, 18) and also with theoretical considerations in view of the sludges possessing a pH of 7-8. Relatedly, Jenkins and Cooper (10) suggested that metals in sewage sludge were present as insoluble sulfides or hydroxides.

TABLE 5. *Soluble concentrations of selected metals in sewage sludge.*

Sludge	ppm[1]		
	Fe	Zn	Cd
Anderson	2.72	0.1	<0.1
Columbus	1.34	<0.1	<0.1
Crawfordsville	0.25	0.1	<0.1
Greencastle	2.27	0.2	<0.1
Kokomo	14.65	0.6	<0.1
Lafayette—2	5.85	0.5	<0.1
Lebanon	8.02	1.6	<0.1
Noblesville	0.69	<0.1	<0.1
Peru	0.01	<0.1	<0.1
Tipton	1.00	<0.1	<0.1

[1]ppm of metal present in a slude filtrate.

Statistical relationships between the concentrations of different chemical components present in sewage sludge were evaluated using linear correlation procedures. The influence of chemical reactions in controlling the total P content of sludge as opposed to biological control of total N is evident by an examination of the respective correlation coefficients[2]: r = < 0.6 for organic C-total P and r = 0.92** for organic C-total N. Correlations between NH_4^+-N and K (r = 0.81**) and Na (r = 0.92**) may be a reflection of their similar solubilities in sludge or of their relative concentrations in raw sewage. Boron and arsenic were highly correlated (r = 0.97**), suggesting the presence of As as a contaminant in B-containing detergents and other laundry products. Since the chemistry of P and As is similar, a significant relationship between P and As was expected and observed (r = 0.89**). The presence of an insoluble Fe-S solid phase is suggested by a correlation between Fe and S (r = 0.79**). Whatever the chemical nature of the insoluble Fe phase, it appears to possess the capacity to retain P (r = 0.69* for Fe-total inorg. P).

Based on the distribution of heavy metals commonly present in plating and other industrial wastes, significant correlations were anticipated between many of the heavy metals analyzed. The following correlations indicate the above to be the case: r = 0.84** for Cu-Pb; r = 0.96** for Cu-Cr; r = 0.65* for Zn-Cd; and r = 0.83** for Pb-Cr. Although essentially all heavy metal sulfides are sparingly soluble, only Hg was related to total S (r = 0.65*).

Based on the results of this study, the approximate amounts of various elements that would be applied to agricultural land can be calculated. The average amounts of selected sludge constituents added by a single 25 ton/acre application of dry sludge (*cf.*, 8) are shown in Table 6. Obviously, a 25 ton/acre application of an average sludge could more than satisfy the N, P, K, Ca, Mg, and S requirements of most agronomic crops. Relatedly, a recent study indicated that sewage sludge was as efficient as commercial fertilizer in supplying nutrients to Coastal Bermudagrass (11). However, the simultaneous application of large amounts of Fe, Cu, Zn, and Cr may result in metal toxicities or induced deficiencies when agronomic crops are grown on sludge disposal sites. For example, individual sludges may contain one of the following; 2% Cr, 3% Zn, 3% Fe, 1% Cu, or 0.2% Pb.

TABLE 6. *Amounts of elements added to soil by a single 25 ton/acre applicationof of sewage sludge.*[1]

Element	Lbs/acre	Element	Lbs/acre
Total N	2400±1500	Mn	36± 22
NH_4—N	920± 920	Cu	140±180
P	1120± 500	Zn	400±440
K	220± 220	Pb	38± 20
Na	400± 440	Cd	8± 12
Ca	4000±1420	Cr	220±300
Mg	580± 190	Ni	52± 64
S	520± 120	B	1± 1
Fe	1040± 460		

[1] Calculated on sludge dry-weight; average ± standard deviation.

[2] Significance of the correlation coefficient (r) is designated by * at P(0.05) and by ** at P(0.01).

Also shown in Table 6 is the standard deviation associated with each sludge constituent. For many elements the variation observed was approximately 100% of the average. Thus, it is likely that a chemical analysis of sludge may be needed before a sound recommendation can be made concerning the rate and frequency of sludge applications to agricultural land. For example, a 25 ton/acre application of sludge may contain 920 lbs of NH_4^+-N, a level of N in excess of that assimilable by plant growth. Similar arguments apply to the amounts of heavy metals added to soils.

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