Heavy Metal Content of Groats and Hulls of Oats Grown on Soil Treated with Sewage Sludges[1]

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ABSTRACT

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Oats (*Avena sativa* L. cv. Noble) were grown on soils treated with air-dried sewage sludge from three Indiana cities. Sludges were applied to a Chalmers silty clay loam soil at rates ranging from 56 to 448 t/ha. Oat samples were separated into groats and hulls, and concentrations of Cd, Zn, Cu, Ni, Fe, and Mn were determined in each fraction by atomic absorption spectrophotometry. The concentration of trace metals in whole oats, groats, and hulls followed a similar pattern and, in general, decreased in the following order: Zn, Fe, Mn, Ni, Cu, and Cd. Except for Mn, the concentrations of trace metals increased with increasing rates of sludge applied. This pattern was similar in oats grown on nonamended and sludge-amended soils. The results indicated that the total intake of trace metals will be similar regardless of whether whole oats or only the groat fraction is consumed. However, the groats contained greater concentrations of Cu, Ni, Zn, Cd, and Mn than the hulls. The Fe content of groats and hulls was approximately the same. The ratio between metal content in groats and that in hulls tended to increase with increasing amounts of sludgeborne metals applied to the soil.

One of the major concerns arising from applications of sewage sludges on agricultural soils is the potential for increased concentrations of potentially toxic metals in crops and subsequently in the human diet. Sewage sludges contain not only macro- and micronutrients required for plant growth, but also toxic metals such as Pb, Ni, and Cd (Page 1974, Sommer 1977). The concentration of metals in crops grown on soils treated with sewage sludge is a complex function of sludge, soil, plant, and environmental factors. This topic has been the subject of several recent reviews (Baker et al 1977; CAST 1976, 1980; Cataldo and Wildung 1978; Chaney and Giordano 1977).

Of the metals applied to soils in sewage sludge, Cd has received the greatest attention because of its uptake by crops and its potential for toxicity to humans and animals (CAST 1980). This concern has resulted in the U.S. Environmental Protection Agency establishing regulations on the amounts of Cd that can be applied to soils used for growing human food-chain crops (U.S. EPA 1979). To minimize adverse effects on crop yields, limiting the total amounts of Zn, Pb, Cu, and Ni applied to soils is also desirable (Knezek and Miller 1976).

The majority of research evaluating the effects of sewage sludge applications on metal concentrations in crops has involved analysis of whole grains, fruits, or tubers. In many cases, grains are processed before they enter human foods. To evaluate the influence of sludge application on metals entering the human diet from grains, the distribution of metals in the various fractions of processed grains must be known in addition to the concentration in the whole grain. Dry milling of corn grain indicates that, of the Zn, Cd, Cu, Ni, Fe, and Mn in the whole kernel, the amounts in the endosperm are 49, 49, 36, 44, 55, and 57%, respectively (Hinesly et al 1979). Similar analysis of wheat grain revealed that amounts in the flour ranged from 14% of the Zn to 55% of the Pb. These authors suggested that sewage sludge additions to soils would significantly increase metal concentrations in the fractions of corn and wheat used in animal rations but only nominally increase metal levels in the fractions of these grains consumed directly by man.

The objective of this study was to evaluate the distribution of metals in oat grain grown on soil treated with municipal sewage sludges.

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MATERIALS AND METHODS

Experimental Design

Field plots were established in the fall of 1976 at the Purdue University Agronomy Farm to evaluate the effect of applying the excessive amount of heavy metals contained in sewage sludge on the yield and composition of several agronomic crops. Sewage sludges selected for study were obtained from sewage treatment plants in Anderson, Marion, and Frankfort, IN. Because these sludges contained elevated levels, significant increases in soil metal concentrations were obtained with sludge application rates of $\leqslant$ 448 t/ha. All sludges were subjected to anaerobic digestion and then dried to approximately 50% solids on sand-drying beds or the equivalent. The composition of the sewage sludges (dry weight basis) is given in Table I. The sludges were applied to the surface of 4.6×12.2-m plots (four replicates) and incorporated into the soil by plowing to a depth of 20 cm. The soil was a Chalmers silty clay loam with the following properties: organic C, 2.3%; total N, 0.18%; cation exchange capacity, 23 meq/100 g; and pH, 5.6. In the spring of 1977, oats (*Avena sativa* L. cv. Noble) were planted and subsequently harvested in late July. No supplemental fertilizer was applied to the plots. Oat grain samples were collected from each replicate plot, dried at 60°C for 48 hr and stored before analysis.

Test Weight

The weight, per Winchester bushel to the nearest 0.1 lb, was determined by method 84-10 of the AACC (1976). The test weight in pounds per bushel was converted to kilograms per hectoliter by multiplying by a factor of 1.29.

TABLE I
Composition[a] of Sewage Sludges

	Source of Sludge		
	Anderson	Marion	Frankfort
Carbon (%)			
Organic	15.40	7.50	10.40
Inorganic	2.03	3.70	1.80
Nitrogen, organic (%)	0.68	0.66	1.42
Phosphorus (%)	1.38	0.85	1.89
Metals (mg/kg)			
Cadmium	284	247	1,210
Nickel	2,040	215	430
Zinc	6,800	5,200	1,900
Copper	1,200	450	1,330
Lead	1,070	1,520	3,480

[a]Dry weight basis.

Processing Procedure

Samples of oats (1,000 g) from each field plot were separated into groats and hulls. A laboratory impact huller (Quaker Oats Co., Barrington, IL) was used to separate the hulls from the groats. The huller produces a mixture of free groats, free hulls, and some unhulled oats. The free hulls were removed by aspiration on a Bates Laboratory Aspirator (Rapsco, Brookshire, TX). The free groats and unhulled oats were then separated on a UNI-FLOW Cylinder Separator model ZS3 (CEA Carter Day Company, Minneapolis, MN) fitted with a number 19-indent cylinder. The oats from this step were returned to the impact huller for a second pass through the process. With these processing procedures, all oat samples were separated into approximately 25% hulls and 75% groats (by weight).

Analytical Procedures

Protein content was determined by the Kjeldahl method as modified by Noel (1979). Ash and moisture contents were determined as described in AACC methods 08-01 and 44-40, respectively (1976).

For metal analysis, samples (2 g $\pm$ 0.01) of ground oats, groats, and hulls were placed in 25 $\times$ 200-mm Pyrex tubes, treated with 10 ml of concentrated HNO_3 and maintained at room temperature for 16–20 hr. The samples were then placed in an aluminum block, initially at room temperature, and gradually heated to 130°C. Heating at 130°C was continued until about 0.25 ml of HNO_3 remained. After cooling the samples, 3 ml of a mixture of 60% $HClO_4$ and concentrated H_2SO_4 (12:1, v/v) was added and the sample was boiled gently in an aluminum block preheated to 210°C until evaporation of the $HClO_4$ was complete. After cooling, the samples were diluted to 10 ml with deionized water. The digests were analyzed for Cd, Zn, Ni, Cu, Fe, and Mn with a Varian AA-6 flame atomic absorption spectrophotometer fitted with a background corrector (used for Cd and Ni).

Appropriate controls and standards were prepared. All reagents were analytical grade, and solutions were prepared with distilled deionized water. Glassware was washed in 10% HNO_3 before use.

RESULTS AND DISCUSSION

The effect of sewage sludge application on the test weights and protein and ash contents of whole oats, groats, and hulls is shown in Table II. The test weights (range of 45.6–48.2 kg/hl) were not significantly altered by sludge additions except for the Anderson sludge applied at 224 and 448 t/ha. As expected, essentially all protein was contained in the groat fraction. The protein content of both whole oats and groats increased with increasing amounts of sludge applied. This result is consistent with increased levels of plant-available N in the soil amended with sludge. The ash content of oats and oat fractions tended to decrease with increasing amounts of sludge applied. These two variables are general characteristics of oats that are useful in evaluating their quality as a feedstuff. As such, sludge applications resulted in beneficial changes, eg, increased protein content. Protein levels were significantly enhanced by all application rates of Frankfort sludge and by the rates of 168 t/ha of Marion sludge and 224 and 448 t/ha of Anderson sludge. Because sludges contain heavy metals that are potentially detrimental to man or animals, adequate evaluation of quality must include the metal content of oats grown on sludge-amended soils in addition to the routinely determined variables.

The metal concentrations of whole oats, groats, and hulls are presented in Table III, which also shows the rate of sludge application and the amount of each metal applied. When the application rates of metals are compared with current recommendations for Zn, Cu, and Ni (U.S. EPA 1977) and regulations for Cd (U.S. EPA 1979), they are often far in excess of those recommended or allowed. The experiment was designed to evaluate the validity of current limits on metal additions to soils through a single application of different sludges, rather than to determine optimum sludge application rates from an agronomic standpoint. As a result, the effects of sludge addition on the metal content of oats are not representative of those occurring when sludge is applied to soils at rates recommended for agronomic crops.

Sludge applications increased the levels of Cu, Ni, Zn, Cd, and Fe (Table III) in whole oats and decreased Mn concentrations. Numerous studies have shown that increases in metal concentrations in various crops are related to the amount of metal applied in sludge and that soil properties, such as pH, strongly influence metal uptake by plants (CAST 1976, 1980; Chaney and Giordano 1977; Sommers 1980). The sludges used in this study contained calcium carbonate, resulting in an increase in soil pH from 5.6 to ~ 7.4. This pH change is undoubtedly responsible for the depressed Mn concentrations in oats grown on sludge-treated plots. Even though the plant availability of Cu, Ni, Zn, Cd, and Fe is also inversely related to soil pH, the amount of these metals applied to soils in a plant-available form must have more than compensated for the decreased availability caused by the increase in pH. More detailed data on the effects of sludge on crop yields (oats, corn, soybeans, and winter wheat) and soil properties will be presented in subsequent articles.

The groats contained greater concentrations of Cu, Ni, Zn, Cd, and Mn than the hulls. The Fe content of groats and hulls was approximately the same. The relative enrichment of metals in the groat fraction of oats was calculated from the data shown in Table III. The ratios of metal in groats to metal in hulls were, in decreasing order: Ni, 3.2; Cd, 2.3; Mn, 2.0; Cu, 1.5; Zn, 1.4; and Fe, 1.2. These values are the averages obtained from all treatments. Inspection of the data reveals that the groats-hulls ratio of metal content tends to increase with increasing amounts of sludgeborne

TABLE II
Test Weight and Protein and Ash Contents of Whole Oats and Oat Fractions

Sludge Applied	Application Rate (t/ha)	Test Weight[a] (kg/hl)	Protein (%)[a,b]			Ash (%)[a]		
			Whole Oats	Groats	Hulls	Whole Oats	Groats	Hulls
None	···	48.1 cd	12.8 ab	15.3 ab	2.3 abcd	3.59 c	2.26 bcd	6.83 f
Anderson	56	46.8 cd	13.0 ab	14.9 ab	2.2 abc	3.57 abc	2.32 cd	6.56 ef
	112	45.6 bc	13.8 bc	16.1 bc	2.6 bcd	3.52 ab	2.36 cd	6.54 ef
	224	44.3 b	15.7 de	19.3 de	3.5 e	3.36 ab	2.01 a	5.74 bc
	448	39.6 a	16.2 e	20.1 e	4.0 e	3.16 ab	2.37 d	4.98 a
Marion	56	47.6 cd	12.4 a	14.1 a	1.9 a	3.44 ab	2.30 bcd	6.35 de
	112	48.2 d	13.1 ab	15.4 ab	2.6 bcd	3.42 ab	2.34 cd	5.99 cd
	168	48.7 d	14.9 c	16.8 c	2.1 ab	3.07 a	2.01 a	5.51 b
Frankfort	56	47.9 cd	15.5 c	17.0 c	2.2 abc	3.06 a	2.22 bc	5.97 cd
	112	46.9 cd	15.6 de	19.0 de	2.9 d	3.21 ab	2.17 b	5.96 cd
	168	45.8 bcd	17.5 d	18.4 d	2.8 cd	3.64 bc	2.25 bcd	6.34 def

[a] For each variable, values in a column followed by the same letter are not significantly different by Duncan's multiple range test ($P = 0.05$).
[b] N $\times$ 6.25.

TABLE III
Concentrations of Metals in Whole Oats and Oat Fractions

Sludge Applied	Application Rate (t/ha)	Applied (kg/ha)	Metal Concentration (mg/kg) in[a] Whole Oats	Oat Groats	Oat Hulls
			Copper		
None	...	...	5.44 a	5.44 a	2.54 a
Anderson	56	67	6.38 ab	6.16 ab	4.70 bcd
	112	134	8.83 c	6.74 abc	4.80 bcde
	224	268	8.70 c	8.78 de	5.45 bcde
	448	536	9.08 c	10.40 fg	5.65 bcde
Marion	56	25	5.95 a	5.72 a	3.48 ab
	112	50	8.20 bc	7.45 bc	5.88 cde
	168	75	7.52 abc	11.00 g	6.98 e
Frankfort	56	74	6.98 abc	7.58 cd	6.30 cde
	112	148	6.10 ab	6.10 a	4.48 abc
	168	222	9.22 c	9.25 ef	6.80 de
			Nickel		
None	...	...	5.31 ab	3.51 ab	1.39 a
Anderson	56	114	10.90 de	10.50 c	1.88 ab
	112	228	13.78 e	16.45 de	2.62 b
	224	457	18.05 f	21.75 e	6.32 c
	448	914	30.85 g	41.80 f	12.22 d
Marion	56	12	3.92 ab	1.85 a	0.92 a
	112	24	3.58 a	2.05 a	1.22 a
	168	36	4.35 ab	2.18 a	1.28 a
Frankfort	56	24	6.75 bc	6.45 abc	1.82 ab
	112	48	9.42 cd	9.00 bc	2.45 b
	168	72	11.90 de	11.58 cd	1.80 ab
			Zinc		
None	...	...	35.0 a	48.8 bc	31.6 a
Anderson	56	381	45.3 cde	48.8 bc	25.9 a
	112	762	53.2 ef	54.0 cd	33.6 a
	224	1,523	55.1 f	59.0 de	49.6 b
	448	3,046	64.7 g	64.4 e	63.9 b
Marion	56	291	30.0 a	34.2 a	26.8 a
	112	582	35.1 a	42.9 b	28.8 a
	168	874	36.4 ab	43.2 b	28.2 a
Frankfort	56	106	43.7 bcd	47.5 bc	32.6 a
	112	213	43.1 bc	45.7 b	31.6 a
	168	320	51.5 def	63.0 e	27.0 a
			Cadmium		
None	...	...	<0.05 a	<0.05 a	<0.05 a
Anderson	56	16	0.44 ab	0.47 b	0.19 a
	112	32	0.68 b	0.92 c	0.28 a
	224	64	1.24 c	1.40 d	0.99 b
	448	128	2.26 d	2.36 e	1.57 c
Marion	56	14	0.14 a	0.20 ab	<0.05 a
	112	28	0.20 a	0.28 ab	0.10 a
	168	42	0.37 ab	0.50 b	0.27 a
Frankfort	56	68	3.86 e	4.29 f	1.62 c
	112	136	4.68 f	4.68 g	1.99 d
	168	203	6.61 g	6.83 h	3.32 e
			Iron		
None	...	...	32.3 ab	28.1 a	23.2 ab

TABLE III (continued)
Concentrations of Metals in Whole Oats and Oat Fractions

Sludge Applied	Application Rate (t/ha)	Applied (kg/ha)	Metal Concentration (mg/kg) in[a] Whole Oats	Oat Groats	Oat Hulls
Anderson	56	···	35.8 abc	31.8 abc	38.2 de
	112	···	48.8 c	48.0 def	43.7 e
	224	···	63.8 d	51.6 f	40.8 de
	448	···	64.8 d	49.6 ef	45.6 e
Marion	56	···	45.3 bc	28.9 ab	28.4 bc
	112	···	35.8 abc	38.7 bcd	41.1 de
	168	···	37.7 abc	36.0 abc	34.6 cd
Frankfort	56	···	37.9 abc	40.2 cde	16.9 a
	112	···	28.3 a	28.2 a	22.9 ab
	168	···	69.5 d	69.2 g	83.3 f
Manganese					
None	···	···	28.6 cd	32.5 cd	25.2 d
Anderson	56	···	30.3 d	30.6 bcd	14.6 abc
	112	···	29.0 cd	35.9 d	20.6 cd
	224	···	22.8 abcd	25.2 abc	12.8 abc
	448	···	27.6 bcd	24.3 abc	19.7 bcd
Marion	56	···	17.4 a	23.3 ab	10.8 ab
	112	···	18.1 a	24.6 abc	8.8 a
	168	···	29.4 d	37.8 d	16.9 abcd
Frankfort	56	···	21.3 abc	23.3 ab	8.1 a
	112	···	16.7 a	17.5 a	9.5 a
	168	···	20.2 ab	24.6 abc	17.1 abcd

[a] For each metal, values in a column followed by the same letter are not significantly different by Duncan's multiple range test ($P = 0.05$).

metals applied to the soil, but exceptions to this general trend can be readily found. Because all oat samples were comprised of approximately 75% groats and 25% hulls, the majority of metals assimilated by oats are contained in the groat fraction. Thus, ash content is not a good indicator of trace metal content in oat fractions. As shown in Table II, the ash content of hulls was approximately 2–3 times that of the groats, whereas all trace metals were present in higher concentrations in the groats.

The concentrations of trace metals in whole oats, groats, and hulls followed a similar pattern. In general, the concentrations decreased in the following order: Zn, Fe, Mn, Ni, Cu, and Cd. This pattern was similar in oats grown on nonamended or sludge-amended soils.

In summary, the processing of oats into groat and hull fractions revealed that sludge applications increased the trace metal concentrations of both fractions. The total intake of trace metals will be similar regardless of whether whole oats or only the groat fraction is consumed. However, total metal content may not be directly and linearly related to bioavailability of a metal (Erdman 1981). Although sludge applications altered the distribution of trace metals in groats and hulls, the changes were relatively minor. To estimate the effect of sludge applications on the metal content of foods prepared from oats, analysis of whole oats will provide a satisfactory indicator of the metal content in all products using only groats. These results are different from those of Hinesly et al (1978), in which the trace metal content of corn and wheat endosperm fractions contained lower metal levels than the bran or animal feed fractions.

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