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NEUTRON ACTIVATION ANALYSIS FOR TRACE METAL CONTENT OF BROOKINGS SLUDGE FOR LAND APPLICATION

BY

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in partial fulfillment of the requirement for the
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1983

NEUTRON ACTIVATION ANALYSIS FOR TRACE METAL CONTENT OF BROOKINGS SLUDGE FOR LAND APPLICATION

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor Date

Head, Physics Dept. Date

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CHAPTER I

INTRODUCTION

Land Application Of Sewage Sludge

Many communities that face a sludge disposal problem have considered land application of sludge as a viable means of disposing sewage sludge produced by wastewater treatment plants. Land application of sludge becomes even more feasible (when compared with alternate methods such as incineration or land fill) as air quality controls become more stringent on incinerator emissions and land fills become less available and more costly to use. In addition, land application is an agriculturally beneficial disposal method since the sewage sludge can be used as a soil conditioner and a nutrient source for plants and crops.

The Federal Environmental Protection Agency (EPA) strongly favors land application of sludge as a disposal method and requires communities to consider the application of sewage wastes to land as one of their alternatives to advanced wastewater treatment in order to be eligible for federal funding to improve sewage wastewater treatment facilities.[1] Although use of sewage sludge on the land has definite benefits, several potential problems may develop when applying this method of disposal. One main concern has been the possibility of toxic metal pollution occurring in the application soils. If high concentrations of zinc, copper, lead, cadmium, etc. are present in the sludge, they may be retained by the soil and accumulate to levels which pose a health risk to the environment.

To minimize risks from sludge application on land it is necessary to impose certain regulations and restrictions on sludge application rates and management techniques. EPA is primarily responsible for most of the regulations and guidelines applied to sludge disposal. Included in these guidelines is the requirement to analyze the sludge for any harmful or potentially toxic contaminants it may contain. Application soils should also be analyzed to establish a base reference before the addition of sludge and to determine any unusually high concentrations of elements that would restrict loading rates.

Scope Of Study

This study was conducted to determine the trace metal concentrations in sewage sludge for the city of Brookings, S.D. Instrumental Neutron Activation Analysis (INAA) was used to determine the trace metal content since this methodology yields accurate, precise results for many elements at one time with a minimum of chemical and physical manipulation. Sludge samples were collected from the wastewater plant of Brookings as were soil samples from farming areas selected as potential sludge application sites.

Standards and samples were irradiated in a TRIGA reactor at Washington State University. The gamma ray spectra were analyzed using a lithium drifted germanium crystal detector and a multichannel analyzer. Thirty two different trace metals were identified and their concentrations determined for both sludge and soil.

CHAPTER II

REVIEW OF THE LITERATURE

Characteristics Of Sewage Sludge

During the process of wastewater treatment, sedimentation tanks are used that leave behind a semi-liquid sludge. Sludge may be defined as a semi-liquid waste having a suspended solids content of at least 2,500 parts per million (ppm) which flows, can be pumped, and exhibits delayed settling characteristics in gravity settlers.[2] Physically, sludge is a brown to black liquid with a thin batter-like consistency and has an earthy odor likened by some to that of crude oil or tar. The chemical and physical composition of sludges may vary, depending upon the size and efficiency of the treatment facility, the size of the community, the number and type of industry in the community, etc. Sludges may be classified according to the stage of treatment or specific process by which they were produced. Some of the more common types of sewage sludges are briefly described as follows:[3]

1.) Primary treatment sludge: Primary sludges result from solids settling out of wastewaters during processing in a primary treatment tank. They are raw, unstable, and require further treatment.

2.) Activated sludge: Activated sludges are produced when effluents flowing off the settling tanks from primary treatment are agitated and constantly supplied with air. These sludges mainly consist of the bodies of organisms which grow and multiply rapidly on the decaying wastes present in the wastewater as aeration proceeds. These organisms settle out as a sludge in final sedimentation tanks and are unstable, still subject to much decomposition. Like primary sludges, activated sludges require further treatment before disposal.

3.) Chemical sludge: Chemical sludges are produced when chemicals like alum, lime, ferric salts, organic polymers, or other settling agents are used during primary or secondary treatment to help precipitate phosphorus and suspended solids during sedimentation periods.

4.) Trickling filter process sludge: Filter sludges are produced when primary effluents are sprayed over deep beds of stone where biological growth takes place on the stone surfaces. A humus type of sludge results which is unstable and requires further treatment.

The previous four types of sludge are produced during the treatment of wastewater and are collected out by the use of sedimentation tanks. These sludges contain organic solids which can undergo further decomposition and stabilization. This decomposition is usually done by further biological treatment. The following two sludge types result from the treatment of mixtures of primary, activated, and trickling filter sludges.

5.) Anaerobically digested sludge: Anaerobic sludges are the most common type of sludge and are produced widely in the U.S. from mixtures of primary and activated sludges, primary and trickling filter sludges, or modifications of these systems. The mixtures are treated in large covered tanks, or digesters, where biological activity occurs in the absence of oxygen. During this digestion process, organic matter is first converted to soluble organic acids and then partially converted to carbon dioxide and methane gas. In efficient systems, a period of 10 to 12 days is sufficient to produce a stabilized sludge.

6.) Aerobically digested sludge: Aerobic sludges are produced by small communities in systems where air is forced through the sludge mass. This process produces the oxidation of biodegradable matter to form a mass of microbial cells followed by further oxidation of that microbial, cellular material. This reduces the volume of sludge and odor potential so that these sludges are acceptable for use on the land as soon as the process is complete.

Municipal sludges normally contain an inorganic mineral fraction along with the organic fraction in the solids portion of the sludge. Anaerobically digested sludges generally contain 5 to 10 percent solids and 90 to 95 percent water. Sludges contain many chemical elements in both organic and mineral form. Many of the important constituents found in primary and digested sludges are listed in Table 1.

While some constituents such as volatile solids, heat of combustion, and nitrogen decrease with digestion, most other constituents tend to be concentrated.

Table 1. Average concentration of constituents in primary and digested sludges from 33 U.S. treatment plants.[4]

Constituent	Raw or Primary (geometric mean*)	Digested or Stabilized (geometric mean*)
	mg/kg except where otherwise noted	
Nitrogen	80,000	37,000
Phosphorus	9,070	16,700
Sulfur	3,100	6,010
Boron	775	380
Cadmium	27	4.3
Cobalt	410	290
Copper	740	1,270
Mercury	8.2	6.5
Manganese	460	475
Nickel	420	530
Lead	1,150	2,210
Silver	355	190
Strontium	175	290
Zinc	1,740	2,900
% Volatile Solids	74.4	51.9
BTU/lb	7,910	5,850

* The _n th_ root of the product of _n_ observed values.

Toxic Elements And Soil Characteristics

In all municipal wastewaters small concentrations of trace elements always exist. They originate from biological material, consumer goods, and wear and tear of metallic items in and around the household. Once in the waste water, trace elements quickly become insoluble in water through inorganic precipitation or surface adsorption on organic solids. During the wastewater treatment, trace elements are largely removed from the discharging effluents and concentrated into the sludge.[5]

The trace elements present in sludges are especially important because many trace elements in minute quantities are essential to biological growth. At high concentrations, however, trace elements become detrimental to organisms. Besides the acute toxicities observed under massive doses and chronic effects due to long-term exposure at sublethal concentrations, there are also indications that some elements may accumulate in certain segments of the environment through chemical immobilization (in soils) or through biomagnification (in plant tissues) and gradually build up to potentially hazardous levels.[6] For example, data in Table 2 indicates the increase of trace elements in the top 30 cm of soil after sludge application, while Table 3 represents data obtained from a study of lettuce grown on sludge treated soil.

Table 2. Increase of trace elements in soils treated with 180 metric tons per hectare of composted sewage sludges.[7]

	SOIL DEPTH					
	0cm - 30cm		30cm - 60cm		60cm - 90cm	
Element	Control	Treated	Control	Treated	Control	Treated
			(ppm)			
Cadmium	0.7	1.3	0.7	0.7	0.8	0.7
Chromium	12.7	23.6	12.3	11.6	13.2	12.2
Copper	15.4	28.3	15.1	13.8	15.6	14.5
Nickel	10.6	14.7	10.4	9.4	10.8	9.9
Lead	13.5	44.8	12.2	12.0	13.2	12.8
Zinc	65.3	95.8	60.2	57.0	61.3	60.0

Table 3. Trace elements in lettuce grown on a sludge amended soil.[8]

Sludge Applied metric ton/hectare	Element Concentration in Plant Tissue			
	Zn	Cu	Cd	Pb
		(ppm)		
0	58.8	6.2	1.9	5.6
11.25	90.7	8.0	2.1	4.4
22.50	141.3	6.0	4.0	5.4
45.00	151.6	6.1	4.1	4.6

Based on the chemistry in soils, elements most likely to pose a serious hazard in land application of sludges are Cd, Cu, Mo, Ni, and Zn. The impact of these potentially hazardous elements on plants grown in sludge cropland may be demonstrated by reduced soil fertility and increased plant uptake of these elements. Experimental data shows that plant species, metal elements, and soil pH all exhibit influences on phytotoxicity and elemental uptake pattern of crops grown in sludge amended soil. In plants, leaves appear to accumulate greater concentrations of trace elements than do fruits or grains. For both tolerant plants and sensitive plants, phytotoxicity and increased uptake of trace elements are more acute in acid soil as compared to calcareous soils.[9]

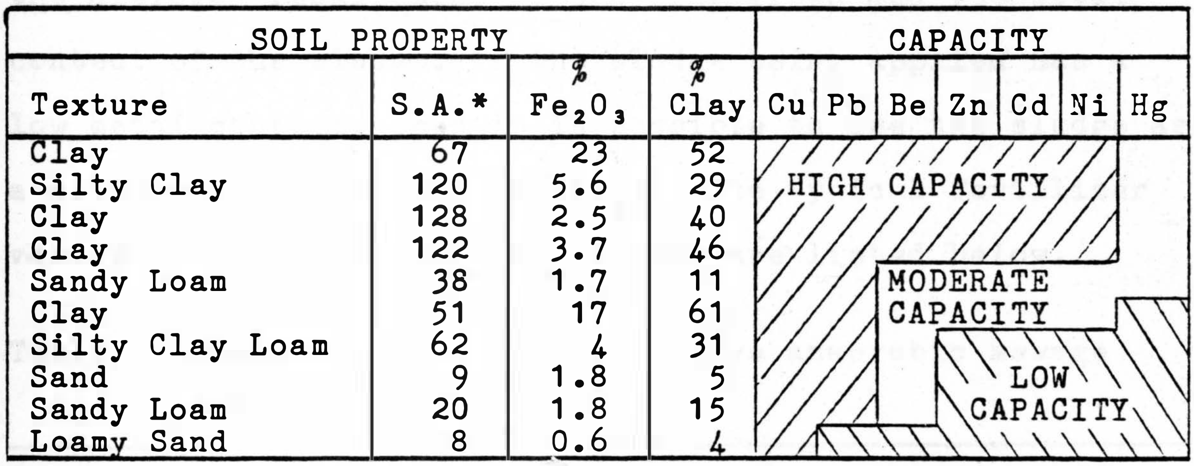
Results of laboratory studies, though limited in their applicability to field situations, have outlined some of the significant factors involved in the attenuation of hazardous elements by the soil. Specifically, they showed that the factors are: kind and concentration of trace elements in the sludge; soil pH; cation exchange capacity; clay content and organic matter content; iron, aluminum, and manganese oxide content; texture, kind and amount of mineral content; oxidation-reduction condition; structure and permeability of the soil. All of these play (together and independently) major roles in determining the fate of trace elements when applied to the soil.[10]

Trace elements such as Ni, Cu, Pb, Zn, Mn, and others exhibit rather high affinities for soil organic matter. More or less stable, soluble and insoluble complexes between these elements and soil organic matter may form. The trace element-organic complexes have not been characterized in detail, but it is generally known that they involve binding of the trace element ion through principally carboxyl and phenolic functional groups in the organic matter.[11]

The pH of the soil solution plays an important part in the relative mobility of many trace elements. The relative mobility of Cd, Ni, Hg, Zn, As, Be, Cr, Cu, Pb, and Se in soils influenced by soil pH are summarized as follows:

In acid soils (pH 4.2 to 6.6) Cd, Ni, Hg, and Zn are "relatively mobile"; As, Be, and Cr are "moderately mobile" and Cu, Pb, and Se are "slowly mobile". In neutral to alkaline soils (pH 6.7 to 7.8) As and Cr are relatively mobile; Be, Cd, Hg, Se, and Zn are moderately mobile and Cu, pb, and Ni are classified as slowly mobile.[12] The preferred soil for land application is usually mineral soil (less than 10 percent organic matter) fine to medium textured (loam or silt loam) and either neutral or alkaline (pH greater than 6.5).[13] Figures 1 and 2 help illustrate the range that exists between soils to attenuate various metal cations and anions.

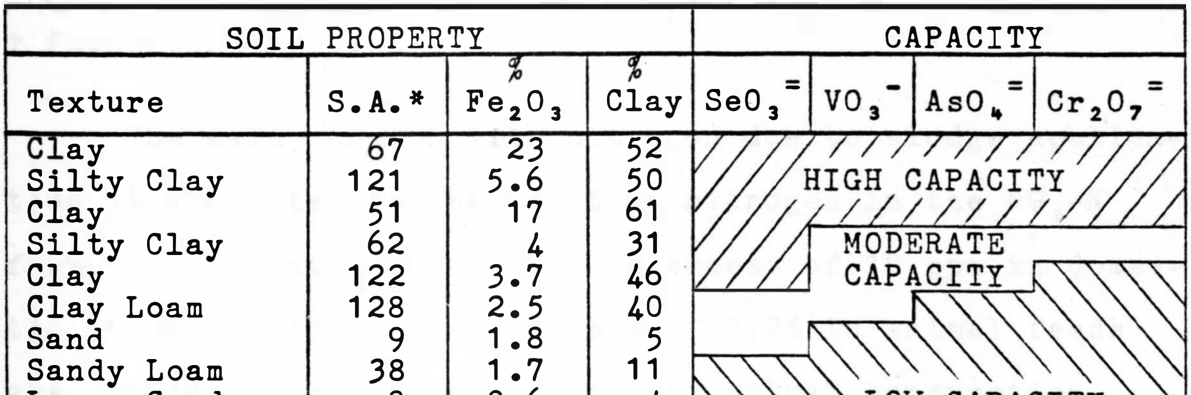
Figure 1. Relative capacity of soils of varying properties for various cations.[14]



SOIL PROPERTY				CAPACITY						
Texture	S.A.*	% Fe_2O_3	% Clay	Cu	Pb	Be	Zn	Cd	Ni	Hg
Clay	67	23	52							
Silty Clay	120	5.6	29							
Clay	128	2.5	40							
Clay	122	3.7	46							
Sandy Loam	38	1.7	11							
Clay	51	17	61							
Silty Clay Loam	62	4	31							
Sand	9	1.8	5							
Sandy Loam	20	1.8	15							
Loamy Sand	8	0.6	4							

* Surface Area (cm^2/gm)

Figure 2. Relative capacity of soils of varying properties for various anions.[15]



SOIL PROPERTY				CAPACITY			
Texture	S.A.*	% Fe_2O_3	% Clay	$SeO_3^=$	VO_3^-	$AsO_4^=$	$Cr_2O_7^=$
Clay	67	23	52				
Silty Clay	121	5.6	50				
Clay	51	17	61				
Silty Clay	62	4	31				
Clay	122	3.7	46				
Clay Loam	128	2.5	40				
Sand	9	1.8	5				
Sandy Loam	38	1.7	11				
Loamy Sand	8	0.6	4				
Sandy Loam	20	1.8	15				

* Surface Area (cm^2/gm)

Nitrogen

The rate of sludge application to land is based on the nitrogen requirement of the crop grown and the metal content of the sludge. If the sludge being applied has a low metal content, then it is possible to use the sludge as a nitrogen fertilizer material.[16] The typical fertilizer values for a representative sludge are listed below.

Table 4. Composition of representative anaerobic sewage sludges.[17]

Component	Range *	Pounds/ton †
Organic Nitrogen	1% - 5%	20 - 100
Ammonium Nitrogen	1% - 3%	20 - 60
Total Phosphorus	1.5% - 3%	30 - 60
Total Potassium	0.27% - 0.8%	4 - 16

* Percent of oven dry solids
† Pound/ton dry sludge

The main concern with nitrogen due to sludge application is the potential hazard from nitrogen in the NO_3-N form. Concentrations of NO_3-N in excess of 10 ppm in domestic water supplies and in excess of 0.2% in animal feeds are considered unsafe for human and animal consumption respectively.[18] The amount of NO_3-N in the soil and that available for ground water pollution are closely related to the biological transformation of N. The N added to aerated soils from organic and inorganic sources is either in the NO_3 form or under aerated soil conditions is converted through mineralization and oxidation to the NO_3 form. In anaerobic soils (water saturated soils with low oxygen content) N is mineralized to NH_3 instead of being oxidized to NO_3 and any NO_3 that was present in the soil is reduced to gaseous N_2O and/or N_2 by microbial processes and released to the air. Crop plants utilize either NH_4 or NO_3 and convert the N into protein. Thus a simple N cycle can be visualized as N input from the sludge that is balanced by 1) harvested crops, 2) leaching of NO_3 in drainage water, and 3) volatilization from the soil as NH_3 or as N_2O and N_2. The capacity of soil for nitrogenous compounds is therefore dependent upon the removal by crops plus that volatilized as NH_3, N_2O, or N_2. The removal of N in harvested crops is usually about 50% of the total input, but this removal can vary from about 25% to 75% depending upon the crop, and the level of N input relative to the crops needs.[19] Thus by proper balancing between the amount of nitrogen added from sludge application and the amount removed from the soil by crop use and volatilization, the amount of NO_3 left available for leaching into the groundwater supplies may be kept at a minimum.

CHAPTER III

METHOD OF ANALYSIS

Introduction

Trace element content of the Brookings sludge and soil samples was determined by the method of Instrumental Neutron Activation Analysis (INAA). INAA was chosen as the means of analysis because it has several advantages when compared with other methods:

1. INAA is non-destructive; thus samples may be stored and re-analyzed in the future.
2. Many elements can be determined at one time. This minimizes the possibility of overlooking a trace element whose role in nutrition and health is unknown at present.
3. A minimum of chemical manipulation is required. This reduces the risk of systematic sample loss and/or contamination by chemical reagents. INAA is an accurate method for trace analysis.
4. INAA is a very sensitive method and has detection limits of less than 1 part per million for many elements.

INAA Theory

Many articles and texts have been written on the subject of neutron activation analysis. The following discussion is meant to give a brief overview of the principles concerning INAA. For a more detailed study, the reader is referred to the text edited by DeSoete, Neutron Activation Analysis, listed in the bibliography at the end of this report.

INAA essentially depends upon the radioactivation of elements and the detection of the gamma radiation given off as the radioactive atoms decay. Activation is generally brought about by the bombardment of the sample with thermal neutrons. Thermal neutrons are neutrons with a mean energy of 0.025 eV which corresponds to the most probable velocity for a Maxwellian distribution at a temperature of 20 degrees Celsius.[20] The majority of the naturally occurring elements can be determined in the part per million (ppm) or even the part per billion (ppb) range with a thermal neutron flux around 10^{12} neutrons per cm^2 per second.[21]

The probability that a particular element may absorb or capture a thermal neutron during irradiation depends upon the nuclear characteristics of the element. This probability for capture is referred to as the thermal neutron cross sectional area, σ, and is usually given in barns (1 barn is equal to 10^{-24} cm^2). The amount of activation of a given element will depend on the number of nuclei present, the cross sectional area of the nuclei, and the intensity of the neutron source used for the irradiation. The number of total target nuclei present for a given isotope is:

$$N = \frac{w\ (f)\ A_v}{M}$$

where N is the number of target nuclei; w is the mass of the given element; f is the natural fractional abundance of the isotope; A_v is Avogadro's number; and M is the atomic weight of the isotope.

If the irradiation is performed in a reactor, the thermal neutrons travel in all directions and the neutron flux is defined as the number of neutrons per second passing in any direction through an area of one square centimeter. For an irradiation with a neutron flux of F on a sample containing N nuclei of a given elemental isotope with cross section σ, the number of reactions per second is:[22]

$$\text{Number of reactions per second} = N\,\sigma\,F$$

Usually the irradiation will produce a nucleus which is radioactive. Elements activated by thermal neutrons generally decay by the emission of an electron (beta decay) with a characteristic half life to a stable daughter element. An illustration of this transformation may be represented by the scheme:[23]

$$(X) \xrightarrow[(n,\gamma)]{\sigma} (Y) \xrightarrow[\beta^-]{t_{\frac{1}{2}}} (Z)\ \text{(stable)}$$

Stable nuclei (X) are activated by thermal neutron capture (cross section σ) and transformed into radioactive nuclei (Y) which decay by beta emission with a half life of $t_{\frac{1}{2}}$ to stable nuclei (Z). An example of this is the activation of sodium:[24]

$$^{23}\mathrm{Na} \xrightarrow[(n,\gamma)]{0.54\ b} {}^{24}\mathrm{Na} \xrightarrow[\beta-]{15\ \text{hours}} {}^{24}\mathrm{Mg}\ \text{(stable)}$$

Normally only a small fraction of the atoms present for each element will experience neutron capture. Therefore, the total number of target nuclei present can be assumed to remain constant unless subjected to intense levels of activation for long periods of time.

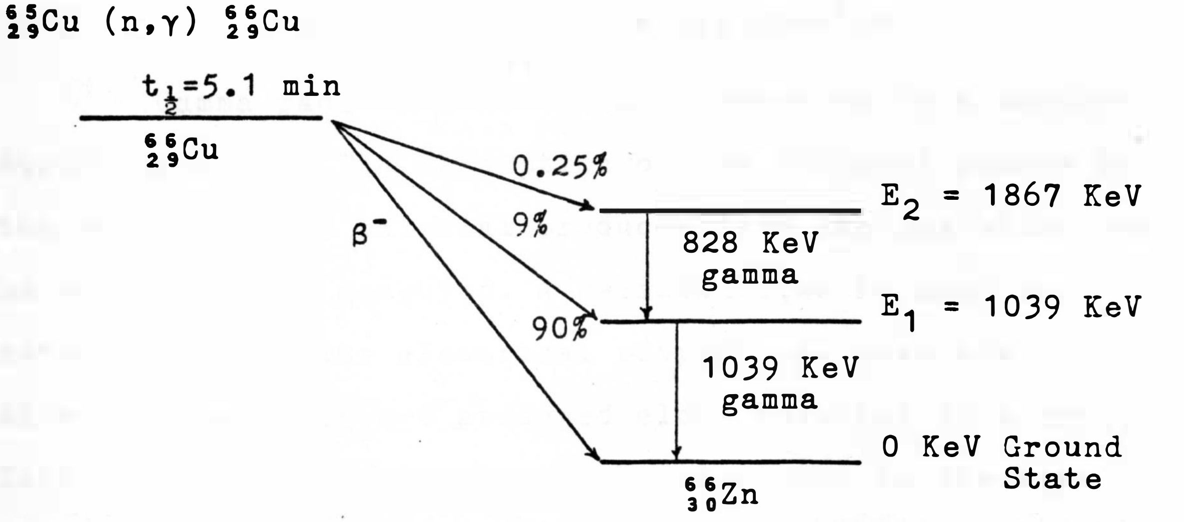
The irradiation time for a sample will depend on the isotopes to be analyzed and their respective half lives. If an isotope containing N target nuclei with cross section σ is placed in a neutron flux F, the number of product nuclei, P_t, with decay constant λ remaining after an irradiation period of t seconds is:[25]

$$P_t = \frac{N\sigma F}{\lambda}(1 - e^{-\lambda t}) = \frac{N\sigma F}{\lambda}(1 - e^{-.693t/t_{\frac{1}{2}}})$$

When the irradiation is performed for a relatively large time t compared to the half life $t_{\frac{1}{2}}$, the exponential term becomes appreciably small and the number of product nuclei will reach a limit, called the saturation point, equal to $N\sigma F/\lambda$. That is, equilibrium is reached in which the rate of production is equal to the rate of decay. An irradiation which lasts for one half life of the product nucleus will produce 50% of the saturation amount, an irradiation of two half lives will produce 75% of saturation, and so on.[26]

Following irradiation and the subsequent beta decay of the radioactive nuclide, the stable nucleus formed may be left in an excited energy state. When this occurs the stable nuclide then returns to the ground state by the emission of one or more gamma rays. The gammas emitted have a discrete energy distribution corresponding to the energy differences between the various energy levels and the ground state of the nuclide. The decay scheme shown in Figure 3 for copper illustrates the different energy levels and the gamma rays that result from the de-excitation of the nuclide after beta decay. The gamma emission from the stable nuclide occurs on the order of 10^{-9} to 10^{-13} second after the initial beta decay.[27]

Figure 3. Decay scheme for ^{66}Cu and the gamma rays that result.[28]

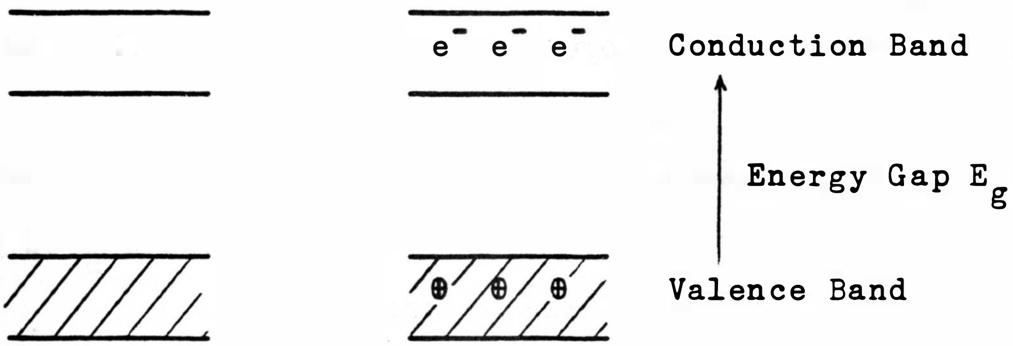


Each radioactive element has its own characteristic gamma ray spectrum, analogous to a fingerprint, and these spectra are used to identify the elements present in the activated sample. A few elements do not emit gamma rays after beta decay (the decay leaves the daughter element in the ground state) and thus can not be detected by INAA. Other elements (mostly of lower atomic mass) form stable isotopes instead of radioactive ones following neutron capture. Since stable isotopes do not decay, they also can not be detected by INAA. However, this is an advantage when analyzing sludge and soil samples. The biological matrix of the sludge and soil consists mainly of hydrogen, carbon, oxygen, and nitrogen. These elements all form stable isotopes when activated and therefore do not contribute any background gammas that might obscure the gamma spectra of the trace elements present.

Detection Of Gamma Ray Spectra

Gamma radiation is normally detected by a semiconductor material. The absorption of the incident gammas in the semiconductor material produces free charges which can be collected and measured. A semiconductor is used as a detector due to its electrical properties. When the atoms of a semiconductor are arranged close together in a crystal lattice, the energy levels of the electrons in the atom split up and give rise to energy bands as is schematically shown in Figure 4.

Figure 4. Electron energy levels in a semiconductor.[29]



Intrinsic Semiconductor at $T = 0^{\circ}$ K

Intrinsic Semiconductor at $T = t^{\circ}$ K

At a temperature of absolute zero, the electrons in a semiconductor fill up completely one or more of the lowest energy levels, the highest filled level being called the valence band. The valence band is separated from the next higher one, the conduction band, by a gap of forbidden energies, E_g, so that no conduction can occur. At any higher temperature, thermal excitation will cause some electrons from the valence band to move into the conduction band, leaving empty places or "holes" carrying a positive charge in the valence band. Excited electrons will fall back to the valence band until a dynamic equilibrium is reached which is a function of temperature. When an electric field is applied to the semiconductor the holes and electrons move to their respective electrodes resulting in conductivity. The absorption of radiation energy creates additional electron-hole pairs and the collection of these charge carriers gives rise to an output pulse. The duration of the pulse depends upon the thickness of the detector and the collection voltage, but it is typically about 10^{-7} to 10^{-8} second.[30] The energy resolution of a semiconductor detector may be expressed as:[31]

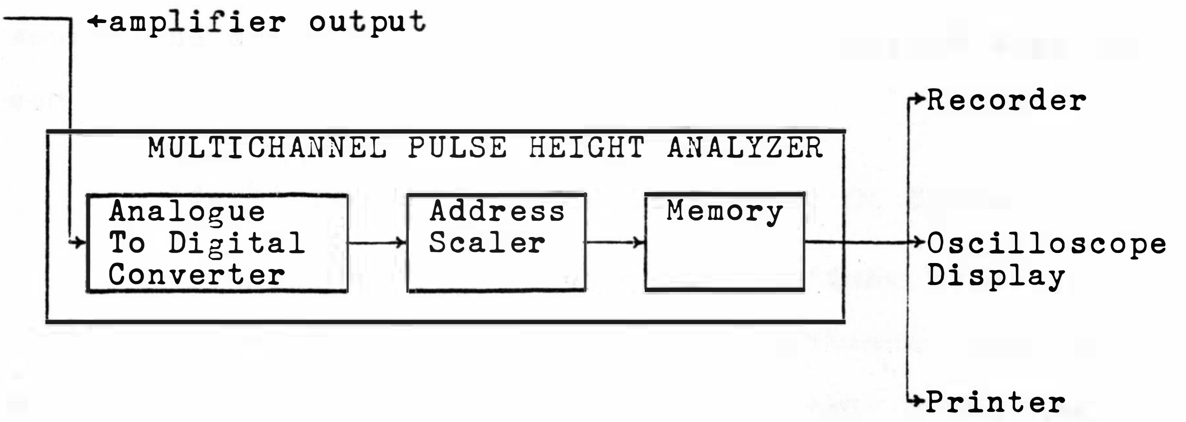
$$\text{Resolution, } \Delta E/E = \sqrt{\varepsilon\Gamma/E}$$

where ε is the average energy loss per ion pair formation, E is the energy of the incident radiation, and Γ is a factor (less than unity) dependent upon the type of semiconductor, known as the Fano factor. Because the energy separation between the valence electrons and the conduction band is small in semiconductors, the average energy loss for each electron-hole pair formed is low (about 3.6 eV in Si and 2.9 eV in Ge).[32] On the other hand, the energy of the incident gamma radiation is on the order of 10^3 to 10^6 eV. Because the average energy loss for ion pair production is extremely small compared to the energy of the incident gamma radiation, semiconductors are capable of excellent energy resolution. For a more detailed discussion on semiconductor detectors, the reader is referred to the text, Introduction to Nuclear Physics and Chemistry by Harvey, listed in the bibliography.

Multichannel Analyzer

Since the output pulses of a semiconductor detector are on the order of millivolts, preamplification of the signal is necessary, followed by the main amplifier which provides additional gain and also controls the pulse shape for optimum working conditions. The output signal is then sent to a multichannel analyzer. The multichannel analyzer makes use of an analogue to digital converter (A.D.C.) and a memory device to allow the simultaneous measurement and storage of the pulse amplitudes. Thus, pulses of different energies are stored as "counts" per channel in the memory. A block diagram of a multichannel analyzer is shown below including some of the auxilary equipment that may be used along with the analyzer.

Figure 5. Scheme of a multichannel analyzer and related equipment.[33]



The use of an A.D.C. implies that a finite recovery time exists for the system after a pulse occurs, depending on the A.D.C. oscillator frequency and the read-in time of the analyzed pulse into the memory. With fast analogue to digital converters (100 MHz oscillator frequency) a recovery time on the order of several microseconds per count can be obtained.[34] While the analyzer is recovering from a count the system is "dead" to further detection. This momentary lapse is termed "dead time" and can be expressed as a fraction of the total analyzer time (live time) used to record counts. The fractional dead time, FDT, is defined as:[35]

$$FDT = DT/CT = (CT - LT)/CT$$

where DT is the total dead time, CT is the actual clock time during the counting and LT is the live time of the analyzer. The fractional dead time may become large when counting short lived isotopes with high activity rates. However, by proper choice of geometry between the activated source and detector, fractional dead time may be kept low and corrected for.

Identification And Quantification Of Elements

By using calibration sources (radionuclides that emit known gamma ray energies) the multichannel analyzer may be calibrated to determine the different gamma ray energies present in the spectra obtained from the activated samples. Once the gamma energies have been determined, the elements present in the sample may be identified. Since the multichannel analyzer records the number of counts for each gamma ray energy determined, elements present can be quantified with the proper use of standards.

The number of counts recorded by the analyzer is proportional to the activity of the sample or standard being counted, namely λP_t. The activity in turn is proportional to the mass of the trace element present in the sample or standard. Thus, a direct proportion may be used to determine the mass of trace element present in the sample based on the known trace element content of the standard, and the ratio of sample to standard counts recorded for each element analyzed. Once the data from the standard and sample counts has been recorded by a memory device (magnetic tape, digital print out, etc.) a computer or programmable calculator may be used to calculate the trace element content of the sample. The amount of trace element in the sample is given by:[36]

$$w_x = \frac{C_x \quad S_s \quad f(t)_s}{C_s \quad S_x \quad f(t)_x} \quad w_s$$

Where w is the weight, x and s refer to the sample and standard respectively, C is the number of counts, S is a saturation factor based on the live count time, and f(t) is the decay factor. S and f(t) are expressed by the equations:[37]

$$S = 1 - \exp(-\lambda LT)$$

and

$$f(t) = \exp(-\lambda\tau)$$

where λ is the decay constant of the isotope of interest, LT is the live count time, and τ is the wait time before the sample or standard is counted. If the neutron flux varies between sample and standard and/or dead time is non-zero during a count, corrections for these variations must also be included and this will yield an overall equation of:

$$w_x = \frac{C_x \quad (1 - e^{-\lambda LT})_s \quad (e^{-\lambda\tau})_s}{C_s \quad (1 - e^{-\lambda LT})_x \quad (e^{-\lambda\tau})_x} \quad \frac{DT_x}{DT_s} \quad w_s \quad f_m$$

where DT and f_m are the dead time and vertical flux correction factors respectively; all other symbols are those defined previously.

Methods Of Analysis For Cd, Pb, And N

Cadmium, lead, and nitrogen are some of the few elements for which INAA is not readily applicable. However, cadmium and lead are trace metals of major concern because of their potential toxicity to animals and humans at elevated levels. Nitrogen is potentially toxic if leached into the ground water in the nitrate form. Nitrogen is also the main nutrient that determines the fertilizer value (along with phosphorus and potassium) of the sludge.

Since Cd, Pb, and N could not be determined by the method of INAA used in this study, values for their concentrations were obtained from two separate and independent analyses performed for Banner Associates of Brookings. Sludge and soil samples were analyzed for cadmium content by Dr. David Hilderbrand of the Chemistry Department at S.D.S.U. The lead and nitrogen content of the sludge was determined as part of a separate analysis done by the Station Biochemistry Laboratory at S.D.S.U.

Both cadmium and lead were determined by the method of flame atomic absorption spectrophotometry. Atomic absorption analysis involves acid digestion of the sludge (or soil) sample which is then aspirated into a flame and atomized. A light beam is then directed through the flame, into a monochrometer, and on to a detector that measures the amount of light absorbed by the atomized element in the flame. For many metals, including cadmium and lead, atomic absorption exhibits sensitive and accurate results. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used for the light beam. The amount of absorption at the characteristic wavelength that takes place is proportional to the concentration of the element in the sample. A more thorough description of flame atomic absorption spectrophotometry may be found in Standard Methods For the Examination of Water and Wastewater 15th edition, 1980, published jointly by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation.

Analysis for nitrogen involves the determination of ammonia nitrogen and total or kjeldahl nitrogen. To determine ammonia nitrogen, a preliminary distillation of a wet sludge sample is required. The distillate is driven off into a solution of boric acid which acts as an absorbent for the ammonia. Titrimetric methods are then used to determine the concentration of the ammonia present in the boric acid solution.

The kjeldahl method determines nitrogen in the tri-negative state. A chemical catalyst is added to the sample of wet sludge to convert the amino nitrogen of organic materials present in the sludge to ammonium sulfate. Any free ammonia or ammonium-nitrogen present in the sample is also converted to ammonium sulfate by the catalyst. The ammonium sulfate is changed to a mercury ammonium complex which is then decomposed to free the ammonia. This ammonia is then distilled off into boric acid and determined by titration with a standard mineral acid. Since the kjeldahl method determines the total nitrogen present in the sample, if the ammonia nitrogen content has been determined previously, the organic nitrogen content may be found by subtraction. The reader is again referred to _Standard Methods For the Examination of Water and Wastewater_ for a more detailed description of the ammonia and kjeldahl methods.

CHAPTER IV

EXPERIMENTAL PROCEDURES

Preparation Of Samples And Standards

The sludge sample was collected on 5/29/1979 from the Brookings old municipal wastewater plant while it was still in use. The digested sludge was taken from the pipe used to fill the sludge truck. The truck had been pumped 3/4 full to make sure the line was thoroughly purged before the sample was taken. The digested sludge was collected in a 500 ml whirlpak and then sharp frozen for preservation.

To prepare the sample for irradiation, the sewage sludge was temporarily thawed, placed into smaller 100 ml whirlpaks and refrozen. Smaller volumes were needed to allow the use of a vacuum freeze dryer to dehydrate the sludge. The use of a freeze dryer for dehydration of the sample was chosen over heat evaporation to prevent any loss of sample material due to volatilization. The resulting solid residue was then recombined and thoroughly mixed. From this mixed solid residue, samples of approximately 250 milligrams each were taken and sealed in high purity polyethylene vials. Sealing of the vials was performed by low heat applied with a small soldering tip. Several vials were prepared to allow the use of duplicate samples for each irradiation run. To test for any background contamination presented by the vials themselves, blank vials were also prepared and analyzed for any significant background effect. The relatively small sample size (250 milligrams) was used due to restrictions on radioactivity levels for the activation analysis technique.

Soil samples were collected on 6/3/1979 from three different sites. For each site, two separate markers were positioned and samples were taken at random from a rough circular area approximately 150 feet in diameter, centered at each marker. Samples were collected with a core sampler to a depth of approximately 6 to 8 inches. Four samples were taken from each quadrant of the circle for a total of 16 samples for each marker area and 32 total for each site. The sites sampled were (1) a field southwest of the Brookings airport termed "active site" where sludge was being applied at that time; (2) a field southwest of the Brookings cemetery termed "used site" where sludge had been applied in the past; and (3) a pasture area south of the Brookings New WasteWater Treatment Plant (NWWTP) termed "new site" where sludge had never been applied. Legal descriptions of the soil sites along with the location of the sample areas used are given in Appendix I.

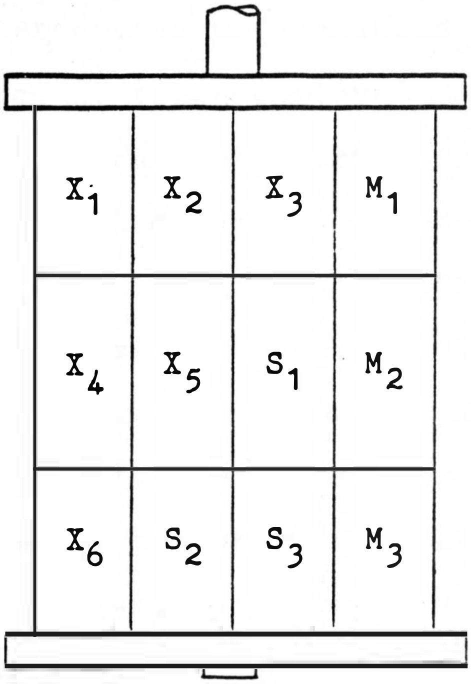
The soil samples for each sample area were kept separate and allowed to dry between sheets of filter paper. These separate groups were then crushed with a wooden roller after drying and then sifted through a #10 sieve followed by a #20 sieve to remove small pebbles and organic matter. The resulting fine silt was then used to prepare several sample vials from each area for irradiation in the same manner as the sludge.

Standards of approximately 250 milligrams each were prepared from the National Bureau of Standards biological and environmental materials; orchard leaf, coal, bovine liver, and fly ash. These standards have been certified by national laboratories using several independent methods of analyses. For the element silver, an Eastman-Kodak standard was used. The Kodak standard consists of a high purity gelatin to which known amounts of metals have been added. The Kodak standard values have also been verified by several nationally recognized laboratories. The standards were sealed in polyethylene vials in the same manner as were the samples.

Irradiation And Counting Of Samples And Standards

Samples and standards used in this study were irradiated in a TRIGA research reactor at the Nuclear Radiation Center, Washington State University under a neutron flux of approximately 6×10^{12} neutrons per cm^2 per second. A steady state operation of one megawatt power output was used for all irradiations performed. Standards and samples were irradiated under virtually identical conditions in groups. Each group consisted of several sample and standard vials assembled together for insertion into the reactor core in a cluster or "packaged" form. The entire package was rotated about a vertical axis during irradiation to cancel out any variations that might have existed in the horizontal neutron flux of the core. Differences in the vertical flux of the core were determined and corrected for with the use of flux monitors placed in the package. A diagram of a sample-standard package is shown below.

Figure 6. Diagram of an irradiation package containing several samples and standards.



$X_{1 \text{ to } 6}$ = sample vials

$S_{1 \text{ to } 3}$ = standard vials

$M_{1 \text{ to } 3}$ = vertical flux monitors

The sample-standard packages were divided into three separate groups for irradiation and analysis based on the product nuclei half lives formed after neutron capture. These divisions were (1) short and very short, (2) intermediate, and (3) long half lives. Standards and samples analyzed for elements with short and very short half lives (on the order of several minutes or less) were irradiated for 10 minutes which produced saturation for several of the elements in this group. If the irradiation time was extended beyond 10 minutes, the samples and standards became too radioactive or "hot" to safely handle during counting or to count with "low dead time". Since the elements in this group decayed away rapidly, samples and standards were counted immediately after irradiation. The count times employed were 4 minutes per sample and standard for the very short half lives and 15 minutes per sample and standard for the short half lives.

Samples and standards analyzed for elements with intermediate half lives (on the order of several hours) were irradiated for 2 hours. After irradiation, the samples and standards were permitted to decay for 36 to 48 hours to allow the short half life elements to decay away to reduce the remaining activity to a safe workable range and minimize "dead time" counting problems resulting from high ^{24}Na activities ($t_{\frac{1}{2}}$ = 15 hours). Samples and standards were then counted for 2000 seconds each since the reduced activity required a longer count time to obtain statistically significant spectra peaks for analysis.

Samples and standards analyzed for elements with long half lives (on the order of several days to several years) were irradiated for a period of 8 hours. After irradiation the samples and standards were allowed to decay for 1 to 2 months to deplete the intermediate and short lived isotopes. Since the remaining activities were largely from low activity, long lived isotopes, long count times of 20,000 to 40,000 seconds were used for samples and standards to obtain suitable spectra for analysis.

The specific nuclear data for all the elements analyzed is given in Appendix II. The short and intermediate counts were completed at Washington State University, while the long counts were conducted at South Dakota State University. Samples and standards from each group were counted under identical conditions to eliminate any variance due to the analyzer system. Identical conditions included keeping the geometry between detector and samples or standards constant, using the same detector system to count samples and standards, and maintaining the same calibration curve and gain settings on the analyzer for each sample and standard group. Any differences in decay times, counting times, and/or dead times between samples and standards were monitored and accounted for.

CHAPTER V

RESULTS ANALYSIS

Trace Element Concentrations

Elemental concentrations for 32 elements in the Brookings sludge determined by this study are displayed in Table 5. The trace element values determined for the six different soil site areas are listed in Table 6. The individual sample values obtained for the sludge and soils are listed in Appendices III and IV respectively.

The statistical uncertainty for the average values given in Tables 5 and 6 is considered in the calculation of s, the standard deviation, listed as the ± values. The standard deviation listed is such that 95% of the trials to determine an elemental concentration would fall within the range of the average from the repeated trials plus or minus two standard deviations. The statistical uncertainty consists in part of:

1. The randomness involved in nuclear counting,
2. The uncertainty in the accepted metal concentrations for the standards.

Statistical methods are employed to determine the uncertainty due to the nuclear randomness involved in counting a sample. For a further discussion on nuclear randomness and its uncertainty, the reader is directed to the chapter on statistical methods in the text edited by DeSoete. The uncertainty in the accepted metal concentrations for the standards is determined experimentally by survey of materials by several independent labs and methods. Sample variation or graininess contributes some uncertainty that is not accounted for in the listed s values. However, uncertainty from graininess is alleviated somewhat by using composite sampling techniques.

The values obtained for the Brookings sludge are comparable to analyses performed on other sludges from communities similar to Brookings. In addition, digested sludge from the New Waste Water Treatment Plant (NWWTP) of Brookings was again analyzed in a separate study done in 1981 for Banner Associates, Inc. This time the analysis was performed by Washington State University using INAA. The values given by the W.S.U. analysis agree favorably with the results determined by this study.

The values obtained for the Brookings soils are also comparable with similar analyses done on other Eastern S.D. soils performed by the Physics Department at S.D.S.U. No large concentration of any trace element was detected in the soil samples that would have any effect on sludge loading rates. Also, the values determined by this study may now be used as a base reference for comparison with future sampling data to monitor any build up of trace metals in the soil due to sludge application.

Table 5. Elemental concentrations for the Brookings, S.D. digested sewage sludge using INAA. (Summer 1979)

Element	Concentration
	(%)
Calcium	5.62 ± .25
Iron	2.03 ± .10
Aluminum	1.68 ± .06
Magnesium	1.26 ± .12
Potassium	.36 ± .03
Sodium	.36 ± .01
Chlorine	.30 ± .03
	(ppm)
Titanium	2680 ± 400
Zinc	1660 ± 90
Barium	1410 ± 170
Copper	1130 ± 140
Manganese	308 ± 10
Chromium	188 ± 10
Strontium	<150
Silver	76.6 ± 12
Molybdenum	<45
Vanadium	43.8 ± 3.2
Nickel	36.2 ± 8.0
Rubidium	22.8 ± 3.6
Mercury	19.7 ± 2.5
Antimony	19.1 ± 1.2
Lanthanum	14.2 ± 1.1
Bromine	12.8 ± 1.2
Selenium	11.8 ± 1.8
Cadmium*	9.1
Arsenic	7.7 ± 0.8
Cobalt	5.8 ± 0.3
Thorium	3.4 ± 0.2
Hafnium	3.2 ± 0.2
Cesium	1.2 ± 0.1
Tantalum	.36 ± .04
Europium	.26 ± .02

* Atomic absorption analysis

Table 6. Elemental concentrations for the Brookings soil areas using INAA. (Summer 1979)

Element	Active Site (Area 1)	Active Site (Area 2)	Used Site (Area 1)
	(%)	(%)	(%)
Aluminum	4.37 ± .15	4.38 ± .15	4.07 ± .13
Iron	1.72 ± .09	1.44 ± .07	1.56 ± .08
Potassium	1.30 ±.024	1.42 ± .03	1.42 ± .03
Magnesium	.86 ± .14	.92 ± .14	.88 ± .14
Sodium	.747 ±.007	.868 ±.008	.868 ±.008
Calcium	.78 ± .10	.81 ± .08	.76 ± .09
Chlorine	<.010	<.010	<.010
	(ppm)	(ppm)	(ppm)
Titanium	2800 ± 600	2110 ± 450	1640 ± 420
Manganese	595 ± 20	680 ± 25	840 ± 30
Barium	732 ± 57	570 ± 46	561 ± 46
Strontium	<275	<275	<250
Copper	<50	<175	<150
Zinc	<50	<50	<50
Rubidium	62.2 ± 4.9	49.6 ± 3.0	47.1 ± 3.7
Vanadium	51.9 ± 4.0	42.2 ± 4.0	44.4 ± 4.5
Chromium	44.0 ± 2.3	34.4 ± 1.8	37.2 ± 2.0
Lanthanum	23.3 ± 1.2	22.0 ± 1.1	23.0 ± 1.0
Nickel	12.9 ± 5.0	12.9 ± 4.5	15.8 ± 6.0
Cadmium	<10	<10	<10
Molybdenum	<3.5	<3.5	<3.5
Silver	<1.0	<1.2	<.99
Cobalt	7.56 ± .39	6.66 ± .34	7.42 ± .38
Bromine	7.1 ± 1.1	5.5 ± 1.2	8.8 ± 1.2
Hafnium	7.00 ± .38	6.11 ± .35	5.28 ± .29
Thorium	7.08 ± .35	5.63 ± .28	6.05 ± .33
Arsenic	6.15 ± .76	4.45 ± .82	5.72 ± .85
Cesium	2.44 ± .15	1.84 ± .11	2.07 ± .12
Europium	.905 ±.051	.800 ±.041	.774 ±.041
Antimony	.632 ±.070	.574 ±.050	.588 ±.056
Tantalum	.60 ± .06	.48 ± .04	.48 ± .04
Selenium	.75 ± .20	.28 ± .15	<.25
Mercury	<.15	<.10	<.10

Table 6. Brookings soil values (continued)

Element	Used Site (Area 2)	New Site (Area 1)	New Site (Area 2)
	(%)	(%)	(%)
Aluminum	3.95 ± .13	3.21 ± .10	2.19 ± .08
Iron	1.56 ± .08	1.26 ± .06	1.02 ± .05
Potassium	1.48 ± .03	.932 ±.034	.608 ±.018
Magnesium	.86 ± .16	2.19 ± .20	1.36 ± .14
Sodium	.962 ±.009	.545 ±.008	.336 ±.004
Calcium	.82 ± .10	10.4 ± .45	16.9 ± .70
Chlorine	<.010	<.010	<.010
	(ppm)	(ppm)	(ppm)
Titanium	1310 ± 250	1740 ± 370	1675 ± 450
Manganese	1010 ± 35	730 ± 25	675 ± 25
Barium	576 ± 48	574 ± 110	555 ± 100
Strontium	<350	<400	<500
Copper	<150	<120	<100
Zinc	<50	<50	<50
Rubidium	45.6 ± 4.0	38.7 ± 4.2	23.0 ± 3.0
Vanadium	46.5 ± 5.2	41.8 ± 3.8	42.8 ± 3.5
Chromium	32.0 ± 1.7	32.0 ± 1.7	24.0 ± 1.3
Lanthanum	22 ± 1	18 ± 2	17.3 ± 1.1
Nickel	14.5 ± 5.0	<10	<10
Cadmium	<10	<50	1.7*
Cobalt	8.26 ± .41	5.38 ± .26	3.76 ± .19
Bromine	8.4 ± 1.3	15.2 ± 1.8	14.2 ± 1.1
Hafnium	5.49 ± .30	4.45 ± .25	3.20 ± .18
Thorium	5.32 ± .26	5.28 ± .27	4.70 ± .24
Arsenic	4.49 ± .96	2.7 ± .90	3.3 ± .60
Molybdenum	<4.0	<50	<50
Cesium	2.04 ± .12	2.13 ± .13	1.69 ± .10
Silver	<.95	<.59	<.52
Europium	.768 ±.042	.553 ±.031	.418 ±.023
Antimony	.690 ±.044	.469 ±.051	.426 ±.047
Tantalum	.50 ± .04	.48 ± .05	.45 ± .05
Selenium	<.25	.91 ± .20	1.22 ± .23
Mercury	<.20	<.10	<.10

* Atomic absorption analysis

Results of the lead and nitrogen analysis by Station Biochemistry at S.D.S.U. are listed in Table 7. The analysis, conducted for Banner Associates, was performed on digested sludge collected on 8/13/1981 from the sludge line to the truck. The solids concentration of the sludge at sampling time was 4.7% which is a common value for the Brookings sludge.

Table 7. Analysis of lead and nitrogen by Station Biochemistry on the sludge from the Brookings NWWTP.[38]

Parameter	Concentration-wet basis	(dry basis)
Lead	1.5 ppm	32 ppm
Total Kjeldahl Nitrogen	0.264 %	5.62 %
Ammonia Nitrogen	0.081 %	1.72 %
Organic Nitrogen	0.183 %	3.90 %

Toxic Metal Loading For Soils

The sludge loading rate methodology preferred by the EPA at present for toxic metals are the guidelines set down by the U.S. Department of Agriculture for cumulative metal addition to the cropland based on soil CEC (cation exchange capacity).[39] Calculations for this method are expressed in the form:

$$T = \frac{500\ Am}{ppm}$$

where Am is the maximum amount of the specified trace metal in lbs/acre that may be applied to the soil over the life span of the disposal site; ppm is the concentration of the trace metal in the sludge in micrograms/gram (dry weight); T is the total tonnage/acre of sludge (dry weight) permitted over the life span of the site; and 500 is a factor to convert ppm to lbs/ton (dry weight). The maximum amounts of trace metal accumulations allowed are listed in the following table.

Table 8. Total amount of sludge metals allowed on cropland.[40]

Trace	Soil Cation Exchange Capacity (CEC)*		
Metal	0 - 5	5 - 15	>15
	Maximum Amount (Am) in lbs/acre		
Lead	500	1000	2000
Zinc	250	500	1000
Copper	125	250	500
Nickel	50	100	200

* meq/100 gm of soil determined by ammonium acetate method

Using the data values for the various metal concentrations, the maximum tonnage (dry weight) may be calculated for each element listed in Table 8 depending upon the soil CEC of the disposal site. Soil CEC was determined for several sites by the S.D.S.U. Water and Soils Laboratory in the study conducted by Banner Associates. The sites analyzed (including the trace metal sites) were found to have a CEC range of 35.4 to 42.7 meq/100 gm soil.[41] This indicates that the highest Am values in Table 8 should be applied to the Brookings sludge. Once the maximum tonnage (T) has been determined, maximum yearly rates (R) may be calculated if the site life span (L) is known (R=L/T). The maximum tonnages of the sludge/acre for Pb, Zn, Cu, and Ni along with yearly rates corresponding to an estimated 20 year life span for disposal of Brookings sludge are listed in Table 9.

Table 9. Maximum amount of Brookings sludge (dry weight) for a site life span.

Trace Metal	Amount Allowed (lb/acre)	Maximum Sludge Tonnage/acre	Maximum Yearly* Rate-Tonnage/acre
Lead	2000	31250	1562
Zinc	1000	301	15
Copper	500	221	11
Nickel	200	2762	138

* Estimated site life span of 20 years.

Cadmium Loading For Soils

Recent interim final regulations by EPA have set down specific limitations on solid waste application to the land based on cadmium content. On land used to produce tobacco, leafy vegetables, or root crops grown for human consumption, annual application of sludge-borne cadmium may not exceed 0.5 kg/ha (0.446 lbs/acre).[42] For other food chain crops, the annual cadmium application rate should not exceed the values listed in Table 10.

Table 10. Annual cadmium application rates.[43]

Time Period	Application Rate kg/ha	(lb/acre)
Present to June 30,1984	2.0	1.784
July 1,1984 to December 31,1986	1.25	1.115
Beginning January 1,1987	0.5	0.446

In addition, EPA has set a maximum cumulative loading of cadmium for a site life span based on soil CEC and pH as shown in Table 11. If the soil is adjusted to pH 6.5 or greater during application of the sludge, and is maintained during the growing season of the crop, then the higher application rates listed in Table 11 may be used for the specific soil CEC range.

Table 11. Maximum cumulative application of sludge-borne cadmium.[44]

	Background Soil $pH<6.5$		Background Soil $pH\geq6.5$	
Soil CEC	kg/ha	(lb/acre)	kg/ha	(lb/acre)
< 5	5	4.46	5	4.46
5 - 15	5	4.46	10	8.92
> 15	5	4.46	20	17.84

In the Banner Associates study, soil pH was found to range from 7.1 to 8.0 for the several disposal sites analyzed.[45] Using this pH data along with the cadmium content of the Brookings sludge, annual and maximum loading rates were calculated for cadmium based on the EPA limits. The results for cadmium loading are given in Tables 12 and 13.

Table 12. Annual maximum loading rates for Brookings sludge based on EPA cadmium standards.

Time Period	Application Rate tons/acre (dry weight)
Present to June 30, 1984	98
July 1,1984 to December 31,1986	61
Beginning January 1,1987	24

Table 15. Maximium amount of Brookings sludge (dry weight) for a site life span based on EPA cadmium standards.

Amount of Cadmium Allowed*	Maximum Sludge Tonnage	Maximum Yearly Rates**
17.84 lbs/acre	980 tons/acre	49 tons/acre †

* Amount allowed for soil CEC $\geq$ 15 meq/100gm soil with background soil pH $\geq$ 6.5.

** Estimated site life span of 20 years.

† 49 tons/acre per year would be valid until 12/31/1986. After this the lower annual rate limit of 24 tons/acre (see Table 12) would apply.

Nitrogen Loading For Soils

Nitrogen loading rates are usually determined by a mass balance equation. The balance equation considers the amount of nitrogen added to and removed from the soil. If the equation is balanced, no net accumulation should occur within the soil. Balance will be determined primarily by the amount of available nitrogen in the sludge, the amount of residual nitrogen in the soil, and the amount of nitrogen removed by crop cover. Balance could also include secondary factors such as nitrogen added by precipitation and removed by leachate. However, the amount of nitrogen added by precipitation is small enough as to be insignificant when compared to the primary factors, and proper balance of the primary factors should result in insignificant losses in leachates. Thus, the secondary factors are omitted and the balance equation, expressed in terms of the primary factors to determine the loading rate, R, is given by:

$$R = \frac{\text{Crop nitrogen requirement} - \text{Residual nitrogen in soil}}{\text{Available nitrogen in the sludge}}$$

Crop nitrogen requirement will depend upon the particular crop grown and the yield desired. For South Dakota, crop nitrogen requirements may range from 30 to 300 lbs/acre. Residual nitrogen in the soil depends upon the decomposition of the organic matter present.

Approximately 1% to 3% of the total organic nitrogen contained within the soil is released by ammonification each year.[46] Ammonification is the process where amines and amino acids are broken down to ammonia (NH_3), which is rapidily converted to ammonium (NH_4^+).[47] Table 14 lists the amount of nitrogen that may be expected due to the breakdown of organic matter.

Table 14. Average nitrogen release expected per year due to the breakdown of organic matter in the soil.[48]

Soil Organic Matter	Percent Organic Matter Breakdown* 1	2	3
%	lbs/acre N released per year		
1	12	26	40
2	26	52	78
3	40	78	120
4	52	104	156
5	66	132	198

* Under normal conditions the expected rate of breakdown is ½% per year for grass sod, 1% to 1½% for small grains and 1½% to 3% for row crops.

Available nitrogen in the sludge is the inorganic nitrogen (Ni) plus 20% of the organic nitrogen (No). 20% is used since research indicates that only 15% to 20% of the organic nitrogen in the sludge is available for use during the first year of application.[49] Available nitrogen from the sludge is then given by:

$$\frac{\text{lbs N}}{\text{ton of sludge}} = \left(\frac{\text{Ni}}{100} \times \frac{2000\text{ lbs}}{\text{ton}}\right) + \left(\frac{\text{No}}{100} \times 0.20 \times \frac{2000\text{ lbs}}{\text{ton}}\right)$$

where Ni and No are the dry weight percentages of inorganic and organic nitrogen in the sludge. The above equation simplifies to:

$$\text{lbs N/ton of sludge} = (\text{Ni} \times 20) + (\text{No} \times 4)$$

As sludge nitrogen content, crop nitrogen requirement, and/or residual nitrogen in the soil vary, so will the corresponding nitrogen loading rate calculated by the mass balance equation. Table 15 lists some calculated loading rates based on a few common values for available sludge nitrogen content and crop nitrogen requirements. The rates listed are valid for sludge that is injected or applied beneath the surface of the soil. Nitrogen loading rates may be safely doubled when the sludge is surfaced applied.[50] The doubled rate takes into account nitrogen losses from the sludge due to demineralization and volatization when the sludge is surface applied. (However, pathogenic and odor problems may arise from surface application of sludge, whereas subsurface injection eliminates these problems.[51])

The values obtained for nitrogen (see Table 7) indicate the Brookings sludge contains 1.7% inorganic nitrogen and 3.8% organic nitrogen on a dry weight basis. Using these values, the available nitrogen of the Brookings sludge is 49.6 lbs N/ton sludge (dry weight). Table

15 indicates the sludge loading rate for nitrogen would vary from 1 to 6 tons sludge/acre for subsurface injection. If the sludge were surfaced applied, the rate would vary from 2 to 12 tons sludge/acre.

Table 15. Sludge loading rates based on nitrogen content of the sludge and nitrogen removal by crop cover.

	Nitrogen Required (lbs/acre)*					
Available Nitrogen	50	100	150	200	250	300
lbs N/ton dry sludge	Sludge Loading Rate - tons/acre †					
26	1.9	3.8	5.8	7.7	9.6	11.5
30	1.7	3.3	5.0	6.7	8.3	10.0
34	1.5	2.9	4.4	5.9	7.4	8.8
38	1.3	2.6	3.9	5.3	6.6	7.9
42	1.2	2.4	3.6	4.8	6.0	7.1
46	1.1	2.2	3.3	4.3	5.4	6.5
50	1.0	2.0	3.0	4.0	5.0	6.0
54	.93	1.8	2.8	3.7	4.6	5.6
58	.86	1.7	2.6	3.4	4.3	5.2
62	.81	1.6	2.4	3.2	4.0	4.8
66	.76	1.5	2.3	3.0	3.8	4.5
70	.71	1.4	2.1	2.8	3.6	4.3
74	.68	1.3	2.0	2.7	3.4	4.0

* Nitrogen required equals crop N needs minus residual N in the soil.

† Sludge loading rate is on dry weight basis for sludge applied beneath the soil surface.

Summary - Most Limiting Factor

After annual application rates based on toxic metals, cadmium, and nitrogen have been completed they are then compared against each other. The most limiting rate from these methods is then used to restrict the maximum amount of sludge that may be applied. The most limiting factor for the Brookings sludge is nitrogen up to the extreme nitrogen loading rates at which point copper may also become a limiting factor. The limiting factors for the different parameters are summarized below in Table 16.

Table 16. Comparison of limiting factors, maximum tonnage per acre per year for Brookings sludge. (Estimated site life span of 20 years)

Limiting Factor	Maximum Yearly Rate (dry weight)
Toxic Metals:	tons of sludge/acre-year
Lead	1562
Zinc	15
Copper	11
Nickel	138
Cadmium (EPA):	
Present to 6/30/1984	49*
7/1/1984 to 12/31/1986	49*
Beginning 1/1/1987	24†
Nitrogen Loading:	1 to 12

* Based on maximum cumulative amount of cadmium for site life span.

† Based on annual application restrictions for cadmium.

CHAPTER VI

LAND APPLICATION OF SLUDGE
CONCLUSIONS & RECOMMENDATIONS

Domestic Sludge

The results of this analysis indicate that the Brookings sludge may be classified as a domestic sludge. This is not unexpected since domestic sludges arise from the treatment of domestic wastewater with no or minimal industrial wastes present as is the case for Brookings. Some common ranges of elemental concentrations in domestic and industrial wastewater sludges are shown in Table 17 along with the corresponding values of the Brookings sludge. Except for a few elements that are marginally above, the Brookings sludge concentrations either fall within or are below the domestic sludge range for the elements listed. In addition, the results of the soil analysis indicate no major build-up of any trace metal has occurred in soils which have received applications of Brookings sludge in the past.

Monitoring And Site Selection

Whenever sludge is applied to the land, a monitoring system is required. Sludge and soil characteristics must be monitored to determine appropriate loading rates and to detect any build-up of toxic metals in the soil that might

Table 17. Elemental ranges of treatment plant sludge (mg/kg dry weight), EPA data,[52] compared with values obtained for Brookings sludge.

Chemical Element	Industrial Wastewater	Domestic Wastewater	Brookings Values
Aluminum	10800-70000	3800-13400	16800
Barium	2600-6400	600-1000	1410
Beryllium	<40-<100	<10-<100	*
Boron	*	50-400	*
Cadmium	<40-200	10-400[a.]	9.1
Calcium	32000-128000	4100-120000	56200
Chromium	1240-2700	50-200	188
Cobalt	<40-500	20-400	5.8
Copper	1640-4700	95-700	1130
Iron	64500-225000	2300-12600	20030
Lead	1280-8300	<200-<500	32
Magnesium	3000-7600	500-5400	12600
Manganese	640-6100	100-300	308
Mercury	0.60-3.0	1.0-11.2	19.7
Nickel	440-2800	110-400	36.2
Phosphorus	12700-38300	2900-19600	26700[b.]
Potassium	1600-4000	400-6000	3600
Silver	200-1680	7-100	76.6
Sodium	800-5400	200-7000	3600
Strontium	80-2100	100-200	<150
Vanadium	100-2000	<500-1000	43.8
Zinc	3200-14000	1000-1800	1660

* Analysis not included.

a. An unusually high value for Cd obtained from only one sludge source.

b. Value obtained from Banner Associates data.[53]

occur. Groundwater supplies must also be monitored to determine any impact from sludge applications and to check that toxic metals and nitrogen compounds remain below safe limits. Monitoring requirements for land application of Brookings sludge established by the South Dakota Department of Water and Natural Resources are listed in Table 18. In this table, the Safe Drinking Water Act (SDWA) elements refer to: arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, nitrate, and fluoride. SDWA toxics refer to: endrin, lindane, methoxychlor, toxaphene, silvex, and 2,4-D.

Table 18. Monitoring requirements for land application of Brookings sludge.[54]

Material - Test	Frequency
Sludge:	
pH	Whenever sludge is hauled
Total Solids	2-4 times/week when hauling
Volatile Solids	2-4 times/month
Total Kjeldahl Nitrogen Total Phosphorus SDWA Elements	Twice a year
Soil:	
pH Potassium Nitrogen Phosphorus	Twice per year during year of application (Spring & Fall)
Selenium Copper	Every five years
Ground Water:	
SDWA Elements SDWA Toxics Fecal Coliform	Twice per year during year of application (Spring & Fall)

Several potential disposal sites have been investigated for application of the Brookings sludge. When choosing an actual disposal site certain site selection criteria should be considered to allow full utilization of the sludge without creating environmental problems. The landscape for a sludge disposal site should be one that approximates a closed drainage system as much as possible. A closed drainage system restricts water flow, and water that does accumulate will pond and evaporate or filter through the soil. A closed system ensures containment of the sludge until the potential pollution factors of the sludge have been removed by physical, chemical, and/or biological reactions with the soil. A closed drainage system also prevents sludge constituents and harmful by-products in the sludge from moving onto adjacent land, into flowing water, or into the ground water.

The slope of the disposal site should be less than 4%; steeper gradients may be acceptable on coarse textured soils or where management practices or application methods reduce erosion hazards.[55] The landscape of a site may have to be diked or physically altered to create a closed drainage system. Diking would also serve as a safety factor to contain run off from snow melt and intense rainfall.

Underground sublayers and strata should also be considered for the site. Strata that are porous or interconnected by fissures could lead to rapid infiltration of liquid runoff from the sludge without adequate soil contact time to effectively filter the liquid. This "short circuited" liquid could pose a serious threat to any immediate ground water supplies. Subsoil pan layers (clay pans, plow pans, silican cemented hard pans, lime cemented hard pans, etc.) will restrict the downward movement of water. If such pans are present near the soil surface they can lead to lateral movement of the sludge liquid called seeps. Such seeps could lead to contamination of the areas surrounding the site. Thus, any disposal site chosen should be free of subsoil pan layers.

Disposal Of Brookings Sludge

The present amount of sludge produced by the Brookings NWWTP is approximately 1,042,500 gallons per year (1981 data).[56] The sludge has an average total solids content of 4.7% which puts the sludge production at about 210 tons/year on a dry weight basis. Over half of the yearly sludge produced is hauled to the city lagoons (which act essentially as drying beds) while the rest of the sludge is applied to the land. The sludge designated for the land is applied during the spring and fall of the year with a 1500 gallon sludge truck that "knifes" the sludge in below the soil surface. Approximately 457,500 gallons of sludge/year is applied to the land and 585,000 gallons of sludge/year is disposed of in the lagoons.[57] On a dry weight basis, the amount of sludge used for land application is currently about 90 tons/year.

The following recommendations are made concerning the Brookings disposal plan. First, since the sludge is entirely suitable for land application, the amount of sludge designated for the land could be increased. Although there is a limit to the amount of sludge that can be physically hauled each fall and spring, a small increase should be possible. The current sludge plan tentatively allows for 15 days each fall and spring for sludge hauling at the rate of ten truck loads (15000 gallons) of sludge per day.[58] The amount of sludge hauled by this schedule is only 44% of the yearly sludge volume produced. If the time for sludge hauling was increased to 20 days each fall and spring, the amount of sludge for land disposal would increase from 44% to 58% of the total yearly volume. Yet, 20 hauling days should allow enough time to apply the sludge before ground freeze-up after crop removal in the fall and to meet crop planting deadlines after winter thaw-out in the spring. Since the sludge is a low base fertilizer material (low nitrogen and potassium with high phosphorus content) that is readily available without the high (and rising) cost of commercial fertilizer; it should seem reasonable to try to use as much of the sludge as possible for land application.

Secondly, it is recommended that zinc and nickel be included in the monitoring system for the sludge and soil.

The list of required monitoring tests does not mention zinc or nickel. However, these two elements are involved in sludge loading criteria and are phytotoxic at elevated levels in the soil. The sludge could be analyzed for zinc and nickel once or twice a year when the SDWA elements analysis is performed. As for the soil, zinc and nickel could be tested every five years along with selenium and copper.

Lastly, it is suggested that the sludge disposed of in the lagoons also be considered for land application after sufficient drying has occurred. The present plan is to deposit the sludge in the lagoons and simply leave it as is. This plan does not allow any use to be derived from the sludge, nor does it take advantage of the drying process that occurs. Currently the sludge has to be applied by special equipment in liquid form that is 95% water. Dried or partially dried sludge is easier and more efficient to handle and may be applied in bulk form with ordinary farm machinery. The bulk sludge could be used as a low grade fertilizer, incorporated into the soil in the same manner as organic fertilizer. However, the dried sludge should still be monitored for toxic elements and nutrient value to determine its suitability and establish appropriate loading rates for land application.

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Appendix I

Soil Site Areas

Site #1: Active Site (southwest of airport)

Owner: City of Brookings

Soil Type: Lishmore Silty Clay Loam

Description: West 1700 feet of S.E. ¼ of section 27 T110N - R50W (115 acres)

Sampling Area 1: 790 ft north of main gate - 440 ft east of west fence line.

Sampling Area 2: 1170 ft north of main gate - 125 ft east of west fence line.

(main gate located 0.5 miles east of intersection of county roads 9 and 18)

Site #2: Used Site (southwest of cemetery)

Owner: B.H. Schaphorst

Soil Type: Hecla Loam

Description: South ½ of N.W. ¼ and North ½ of S.W. ¼ of section 34 - T110N - R50W (80 acres)

Sampling Area 1: 0.2 miles east of drive in on gravel road - 60 ft south

Sampling Area 2: 0.2 miles east of drive in on gravel road - 320 ft south

(drive in located 0.5 miles south of intersection of county roads 9 and 18)

Appendix I (continued)

Site #3: New Site (south of Brookings NWWTP)

Owner: City of Brookings

Soil Type: Volga Silty Clay Loam

Description: West ½ of S.W. ¼ of section 14
T109N - R50W

Sampling Area 1: 0.8 mile south from blacktop road turn off to the NWWTP - 160 ft east of gravel road.

Sampling Area 2: 1.0 mile south from blacktop road turn off to the NWWTP - 250 ft east of gravel road.
(blacktop road is county road 12)

Appendix II

Nuclear Data For Elements Studied

Element	Reaction	Half Life	Energy*
Aluminum	^{27}Al (n,γ) ^{28}Al	2.3 min	1779
Antimony	^{123}Sb (n,γ) ^{124}Sb	60 day	1691
Arsenic	^{75}As (n,γ) ^{76}As	26.3 hr	657 & 559
Barium	^{130}Ba (n,γ) ^{132}Ba	12 day	496
Bromine	^{81}Br (n,γ) ^{82}Br	35.3 hr	777
Cadmium	^{114}Cd (n,γ) ^{115}Cd	53.5 hr	337
Calcium	^{48}Ca (n,γ) ^{49}Ca	8.8 min	3083
Cesium	^{133}Cs (n,γ) ^{134}Cs	2.05 yr	796
Chlorine	^{37}Cl (n,γ) ^{38}Cl	37 min	1642
Chromium	^{50}Cr (n,γ) ^{51}Cr	27.8 day	320
Cobalt	^{59}Co (n,γ) ^{60}Co	5.26 yr	1332
Copper	^{65}Cu (n,γ) ^{66}Cu	5.1 min	1039
Europium	^{151}Eu (n,γ) ^{152}Eu	12 yr	1408
Hafnium	^{180}Hf (n,γ) ^{181}Hf	42.5 day	482
Iron	^{58}Fe (n,γ) ^{59}Fe	45 day	1099 & 1292
Lanthanum	^{139}La (n,γ) ^{140}La	40.2 hr	1596
Magnesium	^{26}Mg (n,γ) ^{27}Mg	9.5 min	1014
Manganese	^{55}Mn (n,γ) ^{56}Mn	2.58 hr	847 & 1811
Mercury	^{202}Hg (n,γ) ^{203}Hg	46.6 day	279
Molybdenum	^{98}Mo (n,γ) ^{99}Mo	67 hr	140
Nickel	^{58}Ni (n,p) ^{58}Co	71.3 day	811
Potassium	^{41}K (n,γ) ^{42}K	12.5 hr	1524
Rubidium	^{85}Rb (n,γ) ^{86}Rb	18.7 day	1078
Selenium	^{74}Se (n,γ) ^{75}Se	120 day	265
Silver	^{109}Ag (n,γ)^{110m}Ag	253 day	938
Sodium	^{23}Na (n,γ) ^{24}Na	15 hr	1368

Nuclear Data (continued)

Element	Reaction	Half life	Energy*
Strontium	$^{86}Sr\ (n,\gamma)^{87m}Sr$	2.85 hr	389
Tantalum	$^{181}Ta\ (n,\gamma)\ ^{182}Ta$	115 day	1221
Titanium	$^{50}Ti\ (n,\gamma)\ ^{51}Ti$	5.8 min	320
Thorium	$^{232}Th(n,\gamma)^{233}Th \xrightarrow{\beta} {}^{233}Pa$	27 day	312
Vanadium	$^{51}V\ (n,\gamma)\ ^{52}V$	3.8 min	1434
Zinc	$^{64}Zn\ (n,\gamma)\ ^{65}Zn$	245 day	1115

* Energy of gamma ray used for analysis (in KeV)

Appendix III

Raw Data Values For Duplicate Samples Of Brookings Sludge Using INAA* (June 1979 Sampling - Truck Outlet)

Element	Sample 1	Sample 2	Average ± s
Cadmium† (ppm)			9.1
Zinc (ppm)	1659	1656	1660 ± 90
Nickel (ppm)	38.3	34.0	36.2 ± 8.0
Copper (ppm)	1260	1000	1130 ± 140
Mercury (ppm)	20.4	19.0	19.7 ± 2.5
Selenium (ppm)	10.0	13.5	11.8 ± 1.8
Arsenic (ppm)	5.6	9.7	7.7 ± .8
Sodium (%)	.36	.36	.36 ± .01
Potassium (ppm)	.34	.38	.36 ± .03
Chromium (ppm)	193	182	188 ± 10
Calcium (%)	5.91	5.32	5.62 ± .25
Magnesium (%)	1.34	1.17	1.26 ± .12
Aluminum (%)	1.79	1.58	1.68 ± .06
Iron (%)	2.04	2.02	2.03 ± .10
Manganese (ppm)	320	295	308 ± 10
Barium (ppm)	1270	1550	1410 ± 170
Silver (ppm)	79.5	73.7	76.6 ± 12
Molybdenum (ppm)	<40	<45	<45
Antimony (ppm)	18.2	19.9	19.0 ± 1.2
Rubidium (ppm)	24.4	21.2	22.8 ± 3.6
Vanadium (ppm)	49.1	38.4	43.8 ± 3.2
Chlorine (%)	.31	.28	.30 ± .03
Strontium (ppm)	<150	<125	<150
Thorium (ppm)	3.4	3.5	3.4 ± .2
Cesium (ppm)	1.1	1.3	1.2 ± .1
Hafnium (ppm)	3.2	3.1	3.2 ± .2
Tantalum (ppm)	.35	.37	.36 ± .04
Titanium (ppm)	2680	2670	2675 ± 400
Cobalt (ppm)	5.9	5.8	5.8 ± .3
Europium (ppm)	.25	.28	.26 ± .02
Lanthanum (ppm)	12.4	16.1	14.2 ± 1.1
Bromine (ppm)	13.2	12.3	12.8 ± 1.2

* Instrumental Neutron Activation Analysis

† Atomic Absorption Analysis

Appendix IV

Raw Data Values For Duplicate Samples
Of Brookings Soil Using INAA*
Active Site : Area 1 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	<6.1	<6.0	<10
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	17.1	8.7	12.9 ± 5.0
Copper (ppm)	<50	<25	<50
Mercury (ppm)	<.15	<.11	<.15
Selenium (ppm)	<.35	.75	.75 ± .20
Arsenic (ppm)	6.59	5.7	6.15 ± .76
Sodium (%)	.792	.702	.747 ±.007
Potassium (%)	1.25	1.34	1.30 ±.024
Chromium (ppm)	44.6	43.3	44.0 ± 2.3
Calcium (%)	.59	.98	.78 ± .10
Magnesium (%)	.69	1.03	.86 ± .14
Aluminum (%)	3.77	4.97	4.37 ± .15
Iron (%)	1.76	1.67	1.72 ± .09
Manganese (ppm)	540	650	595 ± 20
Barium (ppm)	722	743	732 ± 57
Silver (ppm)	<1.0		<1.0
Molybdenum (ppm)	<3.2	<3.2	<3.5
Antimony (ppm)	.613	.652	.632 ±.070
Rubidium (ppm)	69.2	55.2	62.2 ± 4.9
Vanadium (ppm)	41.6	62.1	51.9 ± 4.0
Chlorine (%)	<.010	<.010	<.010
Strontium (ppm)	<240	<275	<275
Thorium (ppm)	6.99	7.15	7.08 ± .35
Cesium (ppm)	2.43	2.44	2.44 ± .15
Hafnium (ppm)	7.02	6.97	7.00 ± .38
Tantalum (ppm)	.74	.47	.60 ± .06
Titanium (ppm)	2300	3300	2800 ± 600
Cobalt (ppm)	7.69	7.44	7.56 ± .39
Europium (ppm)	.951	.859	.905 ±.051
Lanthanum (ppm)	25.5	21.1	23.3 ± 1.2
Bromine (ppm)	6.3	7.9	7.1 ± 1.1

* Instrumental Neutron Activation Analysis

Appendix IV (continued)

Raw Data Values For Duplicate Samples
Of Brookings Soil Using INAA*
Active Site : Area 2 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	<6.6	<6.5	<10
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	12.7	13.1	12.9 ± 4.5
Copper (ppm)	<110	<175	<175
Mercury (ppm)	<.10	<.11	<.10
Selenium (ppm)	<.20	.28	.28 ± .15
Arsenic (ppm)	4.22	4.69	4.45 ± .82
Sodium (%)	.855	.868	.862 ±.008
Potassium (%)	1.35	1.48	1.42 ± .03
Chromium (ppm)	34.5	34.3	34.4 ± 1.8
Calcium (%)	.72	.90	.81 ± .08
Magnesium (%)	.90	.94	.92 ± .14
Aluminum (%)	4.52	4.25	4.38 ± .15
Iron (%)	1.46	1.42	1.44 ± .07
Manganese (ppm)	700	660	680 ± 25
Barium (ppm)	596	544	570 ± 46
Silver (ppm)	<1.2		<1.2
Molybdenum (ppm)	<3.5	<3.5	<3.5
Antimony (ppm)	.576	.572	.574 ±.050
Rubidium (ppm)	45.0	54.2	49.6 ± 3.0
Vanadium (ppm)	42.3	42.0	42.2 ± 4.0
Chlorine (%)	<.007	<.012	<.010
Strontium (ppm)	<280	<230	<275
Thorium (ppm)	5.61	5.65	5.63 ± .28
Cesium (ppm)	1.87	1.81	1.84 ± .11
Hafnium (ppm)	6.44	5.78	6.11 ± .35
Tantalum (ppm)	.45	.52	.48 ± .04
Titanium (ppm)	2460	1760	2110 ± 450
Cobalt (ppm)	6.71	6.60	6.66 ± .34
Europium (ppm)	.770	.831	.800 ±.041
Lanthanum (ppm)	23	21	22 ± 1.1
Bromine (ppm)	5.5	5.5	5.5 ± 1.2

* Instrumental Neutron Activation Analysis

Appendix IV (continued)

Raw Data Values For Duplicate Samples
Of Brookings Soil Using INAA*
Used Site : Area 1 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	<6.6	<6.9	<10
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	17.0	14.7	15.8 ± 6.0
Copper (ppm)	<150	<75	<150
Mercury (ppm)	<.10	<.10	<.10
Selenium (ppm)	<.21	<.21	<.25
Arsenic (ppm)	5.79	5.65	5.72 ± .85
Sodium (%)	.866	.891	.868 ±.008
Potassium (%)	1.36	1.47	1.42 ± .03
Chromium (ppm)	39.4	35.0	37.2 ± 2.0
Calcium (%)	.76	.75	.76 ± .09
Magnesium (%)	.76	.99	.88 ± .14
Aluminum (%)	4.13	4.01	4.07 ± .13
Iron (%)	1.61	1.51	1.56 ± .08
Manganese (ppm)	860	820	840 ± 30
Barium (ppm)	578	544	561 ± 46
Silver (ppm)	<.99		<.99
Molybdenum (ppm)	<3.5	<3.6	<3.5
Antimony (ppm)	.632	.545	.588 ± .06
Rubidium (ppm)	55.4	48.8	47.1 ± 3.7
Vanadium (ppm)	46.8	42.1	44.4 ± 4.5
Chlorine (%)	<.013	<.002	<.010
Strontium (ppm)	<240	<65	<250
Thorium (ppm)	6.47	5.63	6.05 ± .33
Cesium (ppm)	2.06	2.08	2.07 ± .12
Hafnium (ppm)	5.47	5.08	5.28 ± .29
Tantalum (ppm)	.49	.46	.48 ± .04
Titanium (ppm)	1600	1680	1640 ± 420
Cobalt (ppm)	7.46	7.38	7.42 ± .38
Europium (ppm)	.775	.772	.774 ±.041
Lanthanum (ppm)	21	25	23 ± 1
Bromine (ppm)	8.2	9.4	8.8 ± 1.2

* Insrumental Neutron Activation Analysis

Appendix IV (continued)

Raw Data Values For Duplicate Samples
Of Brookings Soil Using INAA*
Used Site : Area 2 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	<7.3		<10
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	13.9	15.1	14.5 ± 5.0
Copper (ppm)	<100	<150	<150
Mercury (ppm)	<.18	<.19	<.20
Selenium (ppm)	<.20	<.24	<.25
Arsenic (ppm)	5.06	3.92	4.49 ± .96
Sodium (%)	.990	.934	.962 ±.009
Potassium (%)	1.55	1.41	1.48 ± .03
Chromium (ppm)	32.4	31.7	32.1 ± 1.7
Calcium (%)	.84	.81	.82 ± .10
Magnesium (%)	.79	.93	.86 ± .16
Aluminum (%)	4.00	3.90	3.95 ± .13
Iron (%)	1.56	1.55	1.56 ± .08
Manganese (ppm)	1100	920	1010 ± 35
Barium (ppm)	564	588	576 ± 48
Silver (ppm)	<.95		<.95
Molybdenum (ppm)	<3.9	<3.9	<4.0
Antimony (ppm)	.685	.695	.690 ±.044
Rubidium (ppm)	35.4	55.9	45.6 ± 4.0
Vanadium (ppm)	47.5	45.5	46.5 ± 5.2
Chlorine (%)	<.007	<.002	<.010
Strontium (ppm)	<210	<350	<350
Thorium (ppm)	5.22	5.41	5.32 ± .26
Cesium (ppm)	2.06	2.02	2.04 ± .12
Hafnium (ppm)	5.34	5.64	5.49 ± .30
Tantalum (ppm)	.49	.52	.50 ± .04
Titanium (ppm)	1280	1340	1310 ± 250
Cobalt (ppm)	8.08	8.45	8.26 ± .41
Europium (ppm)	.800	.737	.768 ±.042
Lanthanum (ppm)	23	21	22 ± 1
Bromine (ppm)	7.9	8.9	8.4 ± 1.3

* Instrumental Neutron Activation Analysis

Appendix IV (continued)

Raw Data Values For Duplicate Samples Of Brookings Soil Using INAA*
New Site : Area 1 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	<55	<52	<55
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	<10	<7.5	<10
Copper (ppm)	<90	<120	<120
Mercury (ppm)	<.10	<.10	<.10
Selenium (ppm)	.88	.94	.91 ± .20
Arsenic (ppm)	<2.4	2.7	2.7 ± .9
Sodium (%)	.561	.531	.545 ±.008
Potassium (%)	.940	.925	.932 ±.034
Chromium (ppm)	30.4	33.7	32.0 ± 1.7
Calcium (%)	10.4	10.4	10.4 ± .45
Magnesium (%)	2.11	2.26	2.19 ± .20
Aluminum (%)	3.33	3.09	3.21 ± .10
Iron (%)	1.25	1.27	1.26 ± .06
Manganese (ppm)	730	730	730 ± .25
Barium (ppm)	474	674	574 ± 110
Silver (ppm)	<.59		<.59
Molybdenum (ppm)	<53	<50	<50
Antimony (ppm)	.478	.460	.469 ±.051
Rubidium (ppm)	35.8	41.6	38.7 ± 4.2
Vanadium (ppm)	40.3	43.2	41.8 ± 3.8
Chlorine (%)	<.008	<.009	<.010
Strontium (ppm)	<400	<380	<400
Thorium (ppm)	6.03	4.54	5.28 ± .27
Cesium (ppm)	2.17	2.09	2.13 ± .13
Hafnium (ppm)	4.25	4.65	4.45 ± .25
Tantalum (ppm)	.47	.50	.48 ± .05
Titanium (ppm)	1770	1710	1740 ± 370
Cobalt (ppm)	5.33	5.44	5.38 ± .26
Europium (ppm)	.560	.546	.553 ±.031
Lanthanum (ppm)	19	18	18 ± 2
Bromine (ppm)	16.5	13.8	15.2 ± 1.8

* Instrumental Neutron Activation Analysis

Appendix IV (continued)

Raw Data Values For Duplicate Samples
Of Brookings Soil Using INAA*
New Site : Area 2 (June 1979 Sampling)

Element	Sample 1	Sample 2	Average ± s
Cadmium (ppm)	1.7†		
Zinc (ppm)	<50	<50	<50
Nickel (ppm)	<8	<7	<10
Copper (ppm)	<95	<50	<100
Mercury (ppm)	<.10	<.10	<.10
Selenium (ppm)	1.05	1.38	1.22 ± .23
Arsenic (ppm)	3.1	3.5	3.3 ± .6
Sodium (%)	.325	.348	.336 ±.004
Potassium (%)	.602	.614	.608 ±.018
Chromium (ppm)	23.8	24.1	24.0 ± 1.3
Calcium (%)	17.3	16.5	16.9 ± .70
Magnesium (%)	1.37	1.35	1.36 ± .14
Aluminum (%)	2.17	2.20	2.19 ± .08
Iron (%)	1.01	1.03	1.02 ± .05
Manganese (ppm)	690	660	675 ± 25
Barium (ppm)	544	567	555 ± 100
Silver (ppm)	<.52		<.52
Molybdenum (ppm)	<44	<46	<50
Antimony (ppm)	.487	.365	.426 ±.047
Rubidium (ppm)	28.5	17.6	23.0 ± 3.0
Vanadium (ppm)	47.8	37.9	42.8 ± 3.5
Chlorine (%)	<.010	<.002	<.010
Strontium (ppm)	<620	<260	<500
Thorium (ppm)	4.96	4.45	4.70 ± .24
Cesium (ppm)	1.64	1.74	1.69 ± .10
Hafnium (ppm)	3.29	3.11	3.20 ± .18
Tantalum (ppm)	.44	.46	.45 ± .05
Titanium (ppm)	1480	1870	1675 ± 450
Cobalt (ppm)	3.69	3.82	3.76 ± .19
Europium (ppm)	.414	.423	.418 ±.023
Lanthanum (ppm)	17.3	17.3	17.3 ± 1.1
Bromine (ppm)	15.4	13.0	14.2 ± 1.1

* Instrumental Neutron Activation Analysis

† Atomic Absorption Analysis