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EFFECTS OF AGING ON LEACHATE CHARACTERISTICS
OF ALKALINE STABILIZED BIOSOLIDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in
the Graduate School of The Ohio State University

by

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1999

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ABSTRACT

Biosolids are often marketed and sold to the general public as commercial fertilizers, soil conditioners, and landfill cover. N-Viro Soil™ (NVS) is one of the products produced from advanced alkaline stabilized municipal biosolids. In the N-Viro process, dewatered municipal biosolids are mixed with alkaline reagents such as cement kiln dust (CKD), lime kiln dust (LKD), coal ashes, and flue gas desulfurization (FGD) byproducts. The final products are solid and granular materials with many desirable soil ingredient properties. The objectives of this study were to; 1) examine the effect of aging on the leachate characteristics of field stockpiled NVS, 2) compare the effect of different alkaline reagents and biosolids types on NVS leachate characteristics, and 3) evaluate mobility of macro and trace elements, anions, and organic compounds in NVS.

Two different types of NVSs, NVS1 (Toledo, OH) and NVS2 (Anderson, IN), were stockpiled in the field and samples were taken over a one year period. Water extracts of the samples were analyzed for chemical characteristics. The initial pH of the extracts was higher than 12 in both NVSs because of the presence of $\text{Ca}(\text{OH})_2$. With the conversion of $\text{Ca}(\text{OH})_2$ to CaCO_3 over time, the pH decreased to an equilibrium value of about 8. The NVS2 extract maintained high pH for three months longer than that of

NVS1 because of the higher Ca(OH)_2 content of CKD used at Anderson. Initial dissolved organic carbon (DOC) was high in both NVS extracts as a result of the high initial pH; DOC decreased as the pH decreased. The extracts had high organic N contents because of the high protein contents of NVSs. The C/N ratio in the extracts was about 4 : 1 through the period of analysis. Fresh NVS extracts had high free NH_3 concentrations which dropped rapidly with time because of the pH decrease and volatilization from the NVS piles. Since NVS1 was made with coal ashes as alkaline reagents, the extracts had high S content, mostly in the form of SO_4^{2-} . The concentrations of SO_4^{2-} increased with time because of the dissolution of CaSO_4 . Both NVS extracts had high Ca concentrations and they decreased by carbonation because the solubility of Ca(OH)_2 is much greater than that of CaCO_3 . High extractabilities of Cu and Ni were due to complexation with high initial DOC concentrations at high pH. Although the NVSs had relatively high contents of Cd, Cr, Pb, and Zn, their concentrations in NVS extracts were very low. The low mobility of these trace elements was attributed to adsorption on mineral surfaces, coprecipitation with many Ca compounds, and precipitation as oxides, hydroxides, and carbonates.

The pH, EC, and concentrations of NH_3 and metals in NVS were too high to allow germination of seeds and plant growth. However, field storage improved the chemical characteristics of NVS by shifting the pH from 12 to 8, dispersing free NH_3 , and suppressing trace element leaching. This study shows that NVS can be safely used as a fertilizer, a soil amendment, and a lime substitute if it is sufficiently aged.

Dedicated to Keiko Yamakawa

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During this dissertation, I got two little presents from God. To my children, Chisato and Kohtaro, I thank them for the great joy they have brought me, and I wish them happy and healthy lives.

To Keiko, my wife, I would like to say "Thank you" from the bottom of my heart for her encouragement, understanding, patience, and her love.

I'm done!

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- 1) A new stereoselective method for synthesis of optically active β -alkylhomoallyl alcohols and γ , δ -epoxy- β -alkyl alcohols, *Tetrahedron Lett.* (1991), 32:371-374.
- 2) Synthesis of optically active γ -cyano- β , γ -epoxy alcohols and secondary γ -cyano allylic alcohols, *Tetrahedron Lett.* (1991), 32:2045-2048.
- 3) Remarkable efficiency in the catalytic asymmetric epoxidation of (D)-3 trimethylsilyl- 2 propen-1-ol, *Synlett* (1991), 11:811-813.
- 4) Efficient synthesis of optically active 3-butene-1,2-diols and 4-heteroatom substituted 3-butene-1,2-diols, *Synlett* (1991), 11:813-815.

FIELDS OF STUDY

Major Field: Environmental Science

Minor Field: Soil Chemistry
Organic Chemistry

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LIST OF ABBREVIATIONS

CCE	calcium carbonate equivalency
CKD	cement kiln dust
C/N	carbon nitrogen ratio
DCP	dicalcium phosphate
DCPDH	dicalcium phosphate dihydrate
DOC	dissolved organic carbon
DPASV	Differential pulse anodic stripping
EC	electrical conductivity
EP	extraction procedure
ESR	electron spin resonance
FA	fulvic acid
FA	fly ash
FBA	fluidized bed ash
FGD	flue gas desulfurization
FT-IR	Fourier transformation infrared
HA	humic acid
HA	hydroxyapatite

IAP	ion activity product
ICP	inductively coupled plasma
LKD	lime kiln dust
NVS	N-Viro Soil™
OCp	octacalcium phosphate
OES	Optical emission spectroscopy
TCLP	toxic characteristic leaching procedure
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TON	total organic nitrogen
WET	California waste extraction test
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Land Application of Biosolids

Disposal of biosolids is a serious problem that every country faces. In the United States, large amounts of biosolids have been produced, especially in the last two to three decades, corresponding to increases in the construction of publicly-owned treatment works (POTW). Biosolids have traditionally been placed in municipal landfills, incinerated, and dumped in the ocean. However, with increasing volumes being produced, these options are not sustainable. Moreover, prohibition of ocean dumping and increasing costs of landfilling and incineration have made land application of biosolids the most attractive method.

Application of biosolids to agricultural land has become not only the most cost effective method, but also an attractive management option that provides agronomic benefits. The organic and nutrient contents of biosolids are valuable for improving degraded agricultural land. Reuse of biosolids for N and P fertilizer replacement has been reported and published (Catroux et al. 1981; Davis et al. 1986; Hucker et al.

1981; Kofoed, 1986; Outwater, 1994; Smith, 1996). Crop productivity can also be increased by the application of biosolids (Clapp, C.E. et al. 1986; Higgins, 1984). The agronomic benefits of biosolids as nutrient sources have been demonstrated and many successful examples of utilization of these materials have been reported (Sloan and Basta, 1995; Edwards et al., 1995; Marx et al. 1995; Lue-Hing et al., 1992).

In addition to valuable organic matter and plant nutrients such as N and P, biosolids contain trace elements that may be harmful for plants and humans. They also contain high levels of pathogens and parasite including bacteria and viruses. Therefore, the primary public concern associated with land application is the mobility and availability of trace elements and the levels of pathogenic microorganisms that could contaminate soil, water, crops, and animals. Many extensive studies have been reported with respect to the mobility of trace metals (Steenhuis et al., 1999; McBride, 1998; Barbarick et al., 1998; Richards et al., 1997; McBride et al., 1997; Dudley et al., 1987) and plant uptake of trace metals (Logan et al., 1997; Sloan et al., 1997; Barbarick et al., 1995; Chaney, 1994; Pierzynski and Schwab, 1993; Chaney and Ryan, 1993). Before the 1980s, most biosolids were digested aerobically or anaerobically to stabilize organic compounds and reduce pathogens. In the 1980s, more advanced technologies were developed for treatment of biosolids to yield a pathogen-free product and stabilize the organic matter in biosolids. The two most common methods are composting and alkaline stabilization. While composting relies on biological decomposition, heat, and drying for pathogen destruction and

stabilization of organic matter, alkaline stabilization utilizes a combination of high pH, heat, and drying to achieve the same purpose.

In recent years, a number of advanced alkaline stabilization technologies have emerged that use additives such as cement kiln dust (CKD), lime kiln dust (LKD), and coal ash with special equipment or processing steps (WEF, 1995). These processes have many advantages. They include complete pathogen destruction and lower capital costs while yielding multiple product markets. Therefore, the final product resulting from the advanced alkaline stabilization technologies is more publicly acceptable than lesser treated biosolids. Currently, biosolids products produced from advanced alkaline stabilization have been successfully used as fertilizers, soil conditioners, and lime substitutes.

1.2 N-Viro Soil™

The N-Viro process is an advanced alkaline stabilization process for municipal biosolids, a technology owned by N-Viro International Corporation of Toledo, Ohio (Burnham et al. 1992; Logan and Burnham, 1995). In this process, dewatered biosolids (either a raw-primary, digested, or activated biosolids) are mixed with alkaline reagents. The solids content of the dewatered biosolids ranges from 15-40 % (Logan and Burnham, 1992), and a number of industrial by-products, such as cement kiln dust (CKD), lime kiln dust (LKD), lime (CaO), flue gas desulfurization (FGD) byproducts, wood ash, and many types of coal ashes can be used as alkaline reagents.

These reagents are used alone or in combination. The stabilization process is based on reactions of the type:

In this reaction, CaO reacts with abundant water in the biosolids to produce calcium hydroxide [Ca(OH)₂]. The product, Ca(OH)₂, is a very strong alkaline material with a pH of more than 12. Since this is an exothermic reaction, the temperature rises. It is controlled in the N-Viro process within the range of 52-62 °C (Smith et al., 1998). Because of the consumption of water through this reaction, the final products become drier. The final water content is less than 50%. The conditions during the process such as high pH, high temperature, and drying allow it to achieve the Class A disinfection standards as classified by the USEPA. The final product, N-Viro Soil™, is a solid and granular material with many desirable properties.

N-Viro Soil™ is currently produced at more than forty locations in the USA, the United Kingdom, Canada, and Australia, and includes biosolids from more than seventy towns. Because of its unique properties, N-Viro Soil has been used as a substitute for agricultural limestone, as a fertilizer, as a soil conditioner, for land reclamation, and for landfill cover (Logan, 1992; Logan and Burnham, 1992; Pierzynski and Schwab, 1993; Sloan and Basta, 1995; WEF, 1994).

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical Characteristics of N-Viro Soil™

2.1.1 pH and Electrical Conductivity

Logan and Harrison (1995) analyzed 28 types of N-Viro Soil™ (NVS) from various operating facilities for their chemical characteristics. The pH of the NVS samples ranged from 7.2 to 12, but most were in a narrow range of 11.5 to 12.2 with a mean of 11.9. This high pH is controlled by $\text{Ca}(\text{OH})_2$ in NVS. Electrical conductivity (EC) was also high (3-15 dS/m), probably due to the high water solubility of $\text{Ca}(\text{OH})_2$. With conversion of $\text{Ca}(\text{OH})_2$ to calcium carbonate (CaCO_3) through storage or land application, both the pH and the EC decreased (Logan, et al., 1995; Logan and Harrison, 1994).

2.1.2 Organic Compounds and Macro Elements

Burnham et al. (1992) reported that total organic carbon (TOC) in NVS ranges from 5 to 12 % on a dry weight basis, depending on the dose rate of alkaline reagents

and the solids content of the dewatered biosolids. Raunkjær et al. (1994) measured concentrations of three major organic compounds including proteins, carbohydrates, and lipids in municipal wastewater. These compounds have also been analyzed for many types of biosolids (Inoue et al., 1996; Woods and Malina, 1965). Since NVS is made from municipal biosolids, it should contain the same types of organic compounds. In the N-Viro process, these organic compounds can be hydrolyzed easily under very strong alkaline conditions to become more water-soluble forms. Polymers are widely used in sludge conditioning, thickening, and dewatering processes. Many different types of polymers are available to improve the effectiveness of each process. Polyacrylamide and positively charged polyamine are the most widely used in wastewater treatment facilities. Humic and fulvic acids have been fractionated from biosolids and biosolids amended soils (Boyd and Sommers, 1990). Riffaldi et al. (1982) characterized humic acids and fulvic acids extracted from ten different types of sludges. Humic and fulvic acid fractions were also extracted from anaerobically digested biosolids (Boyd et al., 1980; Sposito et al. 1976). Thus, NVS should contain many types of organic compounds, but few have been characterized.

NVS contains approximately 1.0-1.5 % total Kjeldahl nitrogen (TKN) (Burnham et al. 1992). High organic N in NVS is probably due to protein content. Under a high initial pH, NH_3 exists as free NH_3 and is easily dispersed into the air. Logan et al. (1989) measured N mineralization from NVS based on laboratory

incubation. This study suggested that about 15-20% of the N was mineralized in 60 days.

The total P content of N-Viro Soil varies from 0.2 to 1.1%, with a mean of 0.4% (Logan and Harrison, 1995). Almost all the P is contributed by the biosolids, probably in the form of organic P and CaHPO_4 . X-ray diffraction has shown the presence of apatite in NVSs, probably from reaction with the alkaline reagents (Logan, 1993). Phosphorus is considered to be immobile because it forms insoluble precipitates and bonds strongly with mineral surfaces.

Ca dominates the chemical characteristics of NVS. Total Ca contents range from 10 to 40 % in the forms of CaCO_3 , CaSO_4 , Ca(OH)_2 , CaO , and $\text{CaMg(CO}_3)_2$, depending on the alkaline reagents used in the stabilization process. The solubility of Ca also depends on the solid phase of Ca forms. Magnesium in NVS is contributed by MgO which is a major component of LKD. Sodium content is relatively low (< 0.3%). Potassium (K) content of NVS varies from 1-3%, depending on dose rate of CKD which contains a high content of mica clay.

The presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) in NVSs has been revealed by X-ray diffraction (Logan, 1993), but little is known about the total S content of NVSs. Coal ashes (fly ash and bed ash) and flue gas desulfurization (FGD) byproducts are used commonly as alkaline reagents in the stabilization process. Since the coal ashes are produced by burning S-rich coal, they contain high levels of S. FGD processes utilize limestone and lime to remove SO_2 from the gases emitted by

burning high-S coals. FGD byproducts contain CaSO_4 , CaSO_3 , CaO , and CaCO_3 (Miller, 1995).

2.1.3 Trace Elements

Trace elements in NVSs are primarily contributed by biosolids and they can be diluted by adding alkaline reagents in the stabilization process. The ratio of alkaline reagents to dry biosolids is typically 1.25-1.50 to 1, depending on the solids content of the biosolids. Therefore, the total contents of trace elements in NVSs are relatively low compared to that of the U.S. biosolids (USEPA, 1990; Logan and Harrison, 1995; Burnham et al. 1994; McBride, 1998; Richards et al. 1997). However, As, Mo, and Se may be high in the alkaline reagents, especially when coal ashes are used. Table 2.1 summarizes the total contents of major trace elements in NVSs.

The dilution of dewatered biosolids by adding alkaline reagents significantly reduces trace element concentrations in NVS. The N-Viro process immobilizes some trace elements by precipitating them as carbonate, hydroxide, phosphate, sulfate, and silicate compounds at high pH. Many types of minerals such as calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), portlandite [$\text{Ca}(\text{OH})_2$], and apatite can coprecipitate with trace metals (Chen et al., 1997; Xu et al., 1994). Moreover, oxides and hydroxides of Al, Fe, and Mn in the alkaline reagents provide adsorption sites for trace elements (Elliott et al., 1986; Benyahya and Garnier, 1999).

Trace Metals	Burnham (1992)	Logan (1995)	Richards (1997)	McBride (1998)		USEPA EQS*
				A	B	
mg/kg						
Cd	9	0.83	1.58	1.25	1.64	39
Co	N/A	N/A	5.18	5.18	N/A	N/A
Cu	80	134	119	119	321	1500
Cr	20-120	94.2	N/A	40.2	42.1	1200
Mo	N/A	1.38	9.8	9.8	78.2	N/A
Ni	35-137	55	12.7	12.7	26.5	420
Pb	100-120	48	N/A	32.8	83.6	300
Zn	350-433	186	115	115	307	2800

*Exceptional Quality Sludge (EQS) metal concentrations as defined by the USEPA 40 CFR part 50 for marketing and distribution.

Table 2.1 Total concentration of trace metals in N-Viro Soil™.

The primary concern regarding trace elements is the bioavailability of harmful elements and their long-term environmental fates. Crop uptake of trace elements in biosolids is the major pathway for human exposure. Many plant uptake studies on NVS application have been reported (Logan et al., 1997a; Logan et al., 1997b; Harrison and Goins, 1994; Pierzynski and Schwab, 1993; Jung and Logan, 1992). The uptake varies with the crop type, trace metal, and cumulative application rate. Among the trace metals, plant uptake is generally the greatest for Cd and Zn and the least for Pb (Page et al., 1987).

Bennett et al. (1989) measured metals extracted from N-Viro Soil using a simulated acid leaching test, a modified USEPA extraction procedure. This study

indicated that there was no significant difference in extractability of Cd, Cu, Cr, and Zn between soils with and without NVS, suggesting decreased mobility of NVS trace elements, even at low pH.

Richards et al. (1997) summarized results of extractability of trace elements in dewatered and composted biosolids, and in incinerated biosolids ashes by using various extraction methods (TCLP, WET, and EP). All the materials were from the same biosolids source. While Cu and Ni showed high mobilities, very little Pb was extracted. Extractability of Cd, Cr, and Zn varied, depending on the biosolids source and extraction methods. They also investigated mobility of trace elements and phosphorus by the TCLP extraction method (Method 1311; USEPA, 1992). This study concluded that the N-Viro process increased the potential mobility of Cu, Ni, and Mo while it decreased the mobility of Zn and P. High mobility of Cu and Ni resulted from dissolved organic matter at high pH because these elements have high affinity for organic complexation. The low P mobility in NVS was the result of precipitation reactions with Ca. McBride (1998) estimated the extractability of trace elements using speciation techniques such as differential pulse anodic stripping voltammetry (DPASV), electron spin resonance (ESR), and computer speciation calculation (MINEQL+). This study indicated that Cu and Ni were mobilized by complexation with dissolved organic matter under high pH, especially by coordination with amines and amino acids because of high affinity of these elements for N-ligands. MINEQL+ also suggested that low solubility of Pb, Zn, and Cd was the result of precipitation as hydroxide or oxide forms at pH 12.

2.2 Chemical Properties of Major Calcium Compounds

As mentioned previously, Ca dominates the chemical characteristics of NVS.

This section discusses chemical properties of major Ca compounds that are predicted to be in NVS. Solubility equilibria of several compounds are given in Table 2.2.

Equilibrium reaction	log K ⁰
$\text{CaO (lime)} + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{O}$	32.95
$\text{Ca(OH)}_2 \text{ (portlandite)} + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O}$	22.80
$\text{CaCO}_3 \text{ (calcite)} + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	9.74
$\text{CaMg(CO}_3)_2 \text{ (dolomite)} + 4\text{H}^+ = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	18.46
$\text{CaSO}_4 \text{ (anhydrite)} = \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.41
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O (gypsum)} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.64
$\text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O (MCP)} = \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	-1.15
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O (brushite)} + \text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O}$	0.63
$\text{CaHPO}_4 \text{ (monetite)} + \text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{PO}_4^-$	0.30

Table 2.2 Equilibrium reactions of major calcium compounds at 25 °C, 1 atm (Lindsay, 1979)

2.2.1 Calcium Oxides and Hydroxides

Some alkaline reagents contain large amounts of lime (CaO). CaO readily reacts with H₂O to produce calcium hydroxide [Ca(OH)₂] (Eq. 2.1). This reaction

contributes to pasteurization of biosolids (section 1.2). In the N-Viro process, all of the CaO is transformed to Ca(OH)₂ after mixing with dewatered biosolids (15-30% solids).

Portlandite [Ca(OH)₂] is a strong alkaline material and has high water solubility. Ca(OH)₂ solutions have a pH of 12.5-13. NVS's high initial pH is contributed by Ca(OH)₂. Under atmospheric conditions, Ca(OH)₂ can be converted into CaCO₃ by carbonation (Eq. 2.2). This is an exthothermic reaction, but the kinetics are limited by concentration of CO₂.

2.2.2 Calcium Carbonates

Calcite (CaCO₃) is a major component of many alkaline reagents such as cement kiln dust (CKD), lime kiln dust (LKD), and flue gas desulfurization (FGD) byproducts. CaCO₃ is also produced by carbonation of Ca(OH)₂ (Eq. 2.2). CaCO₃ is relatively insoluble in water, depending on pH and partial pressure of CO₂. CaCO₃ plays a important role as an adsorbent for trace elements and anions. Phosphate adsorption on CaCO₃ surfaces is well known (Griffin and Jurinak, 1973; Freeman and Rowell, 1981). Zn, Cd, and Mn can also be adsorbed on the surface of CaCO₃ (Jurinak and Bauer, 1956; McBride, 1979, 1980). Calcite can coprecipitate with Mn, Fe(II), Co(II), and Cd by adsorption (Sposito, 1989).

2.2.3 Calcium Sulfates

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the dominant form of calcium sulfate in soils. Formation of anhydrite (CaSO_4) and bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is kinetically unfavorable in normal soils. CaSO_4 and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ have been identified as a dehydration product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ only under very dry conditions (Doner and Lynn, 1989). Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is higher than CaCO_3 , and it is not pH dependent (Eq. 2.3).

Gypsum dissolution may improve soil properties by releasing Ca^{2+} and SO_4^{2-} . These ions can enhance the nutrient status of soils and reduce potentially hazardous ions such as Al^{3+} bound to clay surfaces. SO_4^{2-} can react with Al, Fe or K in the soil solution to precipitate such minerals as alunite [$\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$], basaluminite [$\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$], jurbanite ($\text{AlOH}\text{SO}_4 \cdot 5\text{H}_2\text{O}$), or jarosite [$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$] (Eq. 2.4-2.7) (Sposito, 1989)

Usually, the soil pH change is not significant (< 0.3) with gypsum amendments, but Al concentration in the soil solution may decrease through the above listed reactions. Reduction in Al solubility is a major positive impact of gypsum application in acidic soils.

Zhu and Alva (1993) observed a DOC decrease in sandy soils with FGD amendment, indicating that gypsum flocculates the DOC because of its high ionic strength. DOC is considered to promote the mobility of trace metals, especially Cu and Ni which have a high affinity for organic matter. Therefore, gypsum application may reduce trace metal extractability.

2.2.4 Calcium Phosphates

Solubility of calcium phosphates is relatively high compared with other abundant phosphate minerals, and it is minimal at pH 7-9. There is a well-known sequence of calcium phosphate transformation following the order of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [brushite or dicalcium phosphate dihydrate (DCPDH)] $\rightarrow$ CaHPO_4 [monetite or dicalcium phosphate (DCP)] $\rightarrow$ $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ [octacalcium phosphate (OCP)] $\rightarrow$ $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ [hydroxyapatite (HA)] in the order of high to low solubility (Sposito, 1989; Lindsay et al., 1989). The process of OCP formation from DCP is slower than the formation of the DCPDH to DCP because of low OCP solubility (Eq. 2.10). Generally, when P fertilizer is continuously applied in a field, OCP is stabilized and remains for a long time.

Apatite has been studied for removal of toxic elements from wastewater and polluted aquatic systems (Traina and Laperche, 1999; Chen et al., 1997; Xu et al., 1994; Ma et al., 1993). Heavy metals are immobilized through precipitation as phosphate salts and adsorption on the apatite surface.

2.3 Fate of Trace Elements

Trace element mobility is relatively low in normal soils. Most trace elements are immobilized by adsorption on many types of mineral surfaces, precipitation as oxides, carbonates, and sulfides, and complexation with soil organic matter. Some elements can coprecipitate with minerals by adsorption and inclusion.

This section discusses fate of trace elements by the processes of cation adsorption, anion adsorption, complexation with organic matter, precipitation, and coprecipitation.

2.3.1 Cation Adsorption

Cationic trace metal adsorption commonly occurs on the surfaces of noncrystalline aluminosilicates (allophanes) and oxides and hydroxides of Al, Fe, and

Mn. All these minerals provide a similar type of adsorptive site, a valence-unsatisfied OH⁻ bound to Fe³⁺, Al³⁺, or Mn^{3+, 4+}. The adsorption reaction on these minerals is given by the following equation (Eq. 2.12), where S refers to the mineral surface:

The metal adsorption is pH dependent, and more effective at higher pH. At low pH, surface hydroxyl groups of minerals protonate:

At high pH, those groups deprotonate:

Deprotonated hydroxy groups on the soil surface behave as Lewis bases for metal cations. Therefore, metal adsorption is favorable at high pH. Adsorbed trace elements are relatively stable at higher pH. In contrast, at low pH, H⁺ can easily displace the metals on the adsorption site, and free metal ions are released into the soil solution. The pH effect on metal adsorption depends on the net proton charge changes on the mineral surfaces.

Metals can be adsorbed on one, or possibly two (for divalent or trivalent cations), of the following dissociated groups (Eq. 2.15-2.16).

Electronegativity of the trace metals is an important factor influencing the affinity of adsorption on the mineral surface. Generally, trace elements that have higher electronegativity tend to form stronger covalent bonds with O atoms on any mineral surface. On the basis of electronegativity for common divalent metals, the order of adsorption affinity would be:

However, actual trace metal adsorption affinity varies with the adsorbents (Elliott et al., 1986; McBride, 1994). For example, while Pb and Cu are tightly adsorbed on Fe and Al oxides and silica, Mn oxides have high affinity for Pb, Cu, Mn, and, Co.

2.3.2 Anion Adsorption

Anions may adsorb on positively charged mineral surfaces involving protonated hydroxyl and amino groups, or metal cations. The mechanism of the adsorption is given in the following equations (Eq. 2.17-2.19), where S, A, and M refer to the mineral surface, anion, and metal respectively.

Noncrystalline aluminosilicates (allophanes), oxides and hydroxides of Fe, Al, and Mn provide adsorption sites for anions. The surface reaction is generally written as the following equations, where S refers to surface metals such as Fe, Al, or Mn.

When the anion concentration is very high, the protonation step (Eq. 2.20) is not necessary. Anions can replace OH directly on the adsorption sites (Eq. 2.22).

Equations 2.21 and 2.22 are termed "ligand exchange" reactions because the anion displaces OH⁻ or H₂O from the mineral surface. Generally, low pH promotes anion adsorption because of the protonation of the OH group; displacing -OH₂⁺ from the site is thermodynamically more favorable than exchange with -OH.

Several oxyanions have more than one coordination site, and therefore they can be adsorbed on two sites on the mineral surface, termed as "binuclear reaction" (Eq. 2.23). Borate, phosphate, arsenate, and selenite can undergo the binuclear reaction, and anion adsorption is almost nonreversible because of the high stability of the binuclear complex.

2.3.3 Complexation with Organic Matter

Soil organic matter contains many different types of functional groups such as hydroxyl (-OH), carboxyl (-COOH), phenolic (Ar-OH), amine (-NH₂), carbonyl (C=O), and sulfhydryl (-SH) groups. All these groups behave as Lewis bases during complexation with metals. Generally, the Lewis base strength depends on the "hardness" of the binding elements in the order of O > N > S (oxidation state of S is -2). For example, "hard" acids like Ca²⁺ or Mg²⁺ complex with "hard" bases like O-containing groups such as carboxylate. In contrast, Pb²⁺, Hg²⁺, and Ag⁺, are "soft" acids, and tend to form strong complexes with S²⁻-containing groups.

Some trace elements have a high affinity for organic matter and form stable metal-organics complexes. There is a well-known affinity series for divalent transition metals, which have between 0 and 10d electrons, to organic matter. The Irving-Williams order is:

* This series is ordered by atomic number in transition metals.
Affinity of Zn is close to Ni or Co, depending on the organic ligands.
(Stumm and Morgan, 1981)

According to this order, Cu strongly bonds to organic matter and forms the most stable complexes. Electronegativity is related to the complexation strength with organic matter. A typical affinity sequence of metals for soil organic matter at pH 5 is closely related to their electronegativity (Table 2.3). Since metals with high

electronegativities can draw electrons from Lewis bases, they can have strong bonds with "softer" bases. For example, Cu^{2+} and Ni^{2+} , which are "softer" acids with very high electronegativity, tend to complex with amine groups, a less "hard" base, in soil organic matter.

Affinity sequence	Cu > Ni > Pb > Co > Ca* > Zn > Mn > Mg							
Electronegativity	2.0	1.91	1.87	1.88	1.00	1.65	1.55	1.31

*The affinity of humus for the essential macronutrients, Ca^{2+} and K^+ , is (fortunately for plants and animals) higher than electronegativity would predict, suggesting that certain complexing or chelating groups in humus select for these metals on the basis of ionic size.

Table 2.3 Observed order of affinity of divalent metal ions for soil organic matter (at pH 5) related to electronegativity (McBride, 1994).

2.3.4 Precipitation

Precipitation occurs when the concentrations of ions in solution exceed the solubility product of a solid. The precipitation-dissolution status of the solution phase can be quantified by comparing the ion activity product (IAP) to the solubility product of the solid (K_{so}). The dissolution reaction of a solid M_aL_b , is expressed as follows:

the IAP is defined by the equation:

$$\text{IAP} = (\text{M}^{m+})^a (\text{L}^{l-})^b \quad (\text{Eq. 2.25})$$

The relative saturation value indicates if the dissolution reaction is at equilibrium or not, and is given by Ω :

$$\Omega = \text{IAP}/K_{\text{so}} \quad (\text{Eq. 2.26})$$

Since K_{so} is constant for every mineral under standard conditions (usually 25°C, 1 atm), Ω is obtained by measuring the actual concentration of the ions. $\Omega = 1$ means that the dissolution reaction is at equilibrium. If Ω is less than 1, the solution is supposed to be "undersaturated", if Ω is more than 1, it is "supersaturated". Ω is termed the "saturation index", and can be calculated using chemical speciation programs like MINTEQ.

The precipitation of mineral forms is common for relatively abundant elements such as Al, Ca, Fe, Mg, Mn, and Si. For most trace elements, however, adsorption is more probable than precipitation because of their low concentrations in soil.

2.3.5 Coprecipitation

Coprecipitation is defined as "the simultaneous precipitation of a chemical element with other elements by any mechanism and at any rate." (Sposito, 1983). In the presence of mixed solid phases, the low concentration trace elements can be immobilized by coprecipitation with high concentrations of other components, usually abundant elements such as Al, Ca, Fe, Mg, Mn, and Si. For example, Mn, Fe(II),

Co(II), or Cd coprecipitate with Ca by adsorption onto calcite. While Mn, Fe, Co, and Cd easily enter the calcite structure because of similar radii, Cu and Zn, which have smaller radii, do not. Trivalent trace metal ions like Cr^{3+} , Mn^{3+} , and V^{3+} tend to coprecipitate with Al^{3+} and Fe^{3+} oxides and hydroxides. Co tends to be associated with Mn oxides in soils by substitution into octahedral sites. While small divalent cations like Zn and Cu coprecipitate with Al hydroxide, larger cations like Pb and Mn do not. Consequently, size and valence are important factors for coprecipitation. Table 2.4 shows examples of trace elements that coprecipitate with several soil minerals and organic matter.

Solid	Coprecipitated trace elements
Fe and Al oxides	B, P, V, Mn, Ni, Cu, Zn, Mo, As, Se
Mn oxides	P, Fe, Co, Ni, Zn, Mo, As, Se, Pb
Ca carbonates	P, V, Mn, Fe, Co, Cd
Illites	B, V, Ni, Co, Cr, Cu, Zn, Mo, As, Se, Pb
Smectites	B, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb
Vermiculites	Ti, Mn, Fe
Organic matter	Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb

Table 2.4 Trace elements coprecipitated with secondary soil minerals and soil organic matter (Sposito, 1989).

2. 4 Objectives of this study

Many studies have investigated the N-Viro stabilization processes, chemical and physical characteristics of NVS, and effects on crops. However, very little is known about the chemical speciation of NVS and the long-term effect of land application of this material on soil chemical characteristics; which chemical reactions take place, which species are dissolved or precipitated, how those factors change with time, and how different alkaline reagents affect the chemical characteristics. Also, no study has been conducted characterizing organic compounds.

The purpose of this study was to evaluate the speciation of field stockpiled NVS over time. The specific objectives were to: 1) examine the effect of aging on the leachate characteristics of field stockpiled NVS, 2) compare the effect of different alkaline reagents and biosolids types on NVS leachate characteristics, and 3) evaluate mobility of macro and trace elements, anions, and organic compounds in NVS.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Two different types of NVSs were used in this study (Table 3.1). One was obtained from the Bayview N-Viro facility in Toledo, Ohio. The other was obtained from the City of Anderson, Water Pollution Control Utility in Indiana. These materials are respectively referred to as NVS1 and NVS2. NVS1 is made from anaerobically digested biosolids with a combination of fluidized bed ashes (FBA), lime kiln dust (LKD), and non-reactive fly ash (FA). On the other hand, NVS2 is produced from a mixture of raw primary and waste activated biosolids with cement kiln dust (CKD) as an alkaline reagent. The dose rates of alkaline reagents at each facility are shown in Table 3.2.

	NVS1	NVS2
Source	Toledo, OH	Anderson, IN
Biosolids	Anaerobic digested biosolids	30% primary biosolids 70% activated biosolids
Alkaline Reagent	FBA/LKD/FA ¹⁾	CKD ²⁾
Solids (%)	58.3 ~ 59.1	68.6 ~ 70.7
End Use	Ag-Lime, Topsoil	Landfill cover, Ag-Lime

1) FBA: Fluidized Bed Ash; LKD: Lime Kiln Dust; FA: Fly Ash

2) CKD: Cement Kiln Dust

Table 3.1 Sources of N-Viro Soil™ samples used in this study.

N-Viro Soil	Percent by wt.
NVS1 (Toledo)	
• Dewatered biosolids (24 % solids)	50
• Michigan State FBA	25
• Martin Marietta LKD	20
• Wyandotte Michigan dead FA	5
NVS2 (Anderson)	
• Dewatered biosolids (19 % solids)	50
• CKD	50

Table 3.2 Dose rates of dewatered biosolids to alkaline reagents in the N-Viro stabilization processes.

3.2 Sampling

3.2.1 NVS Samples

The two NVSs were stockpiled in the field at the Agronomy Farm, The Ohio State University, Columbus, in June, 1997. Each pile was approximately 2 m long, 1 m wide, and 0.5 m high. In this study, 11 samples were collected monthly from the interior of these piles, approximately 15 cm deep, at 4 different places in each. The NVS samples were kept at 5 °C for further analysis.

3.2.2 Soil Samples

After 12 months of field storage, the two NVS piles were removed, and soil samples were collected from the areas beneath the NVS piles. Soil cores were taken at three different points in each area, and divided each into four sections (0-5, 5-15, 15-30, and 30-60 cm). After air drying, the soil samples were mixed well and analyzed for chemical characteristics. Analysis of variance (ANOVA) was performed using a statistics software MINITAB to determine the significance of treatment and depth.

3.3 Solids Content

Approximately 10 g NVS sample was accurately weighted into a metal cup and dried in an oven at 110 °C for 24 hrs. After cooling, the cup was weighed. Solids content was calculated as a percentage of total sample weight.

3.4 X-Ray Diffraction

NVS sample was analyzed for crystalline mineral phases by X-ray diffraction (XRD). The sample was ground with a mortar and pestle and placed in back-filled, randomly-oriented powder mounts. All XRD analysis was performed with a Philips X-ray diffractometer using Cu K α radiation at 35 kV and 20 mA. The XRD patterns were obtained using a step scanning technique with a fixed time of 4s per 0.05° 2 θ from 15-80° 2 θ .

3.5 Extraction

Water extract of NVS sample was collected by using a mechanical extractor (Model 24-01, Centurion International Inc., Lincoln, NE) using a 60 mL syringe (Fig. 3.1) (Jaynes and Bigham, 1986). 10 g of NVS on dry weight basis was placed in the sample tube. Approximately 55 mL of water extract was collected over 12 hrs. The solid/solution ratio was about 5.5. The NVS extract was kept at 5 °C for further analysis.

3.6 pH

3.6.1 NVS Extracts

The pH of NVS extract was determined with a digital pH/conductivity meter (Model 50, Denver Instrument Company, Arvada, CO) by inserting an electrode into the extracts. The measurement was done just after the extraction.

Fig. 3.1 Cross section of mechanical extractor (Jaynes and Bigham, 1986)

3.6.2 Soil Samples

Soil pH was determined from a 1:1 ratio of soil to deionized water by using a digital pH meter (McLean, 1982).

3.7 Electrical Conductivity

3.7.1 NVS Extracts

The electrical conductivity (EC) of the NVS extracts was determined with a digital pH/conductivity meter (Model 50, Denver Instrument Company, Arvada, CO) just after the extraction.

3.7.2 Soil Samples

A mixture of soil and deionized water (1:5 ratio by weight) was shaken on a mechanical shaker for 1 hr and centrifuged at 3500 rpm for 12 min. The EC was determined with a digital pH/conductivity meter by inserting the electrode into the supernatant.

3.8 Calcium Hydroxide

The calcium hydroxide (hydrated lime) content was measured by the "rapid sugar test method." (ASTM, 1993). 1 g of dried NVS sample was finely pulverized and placed into a 125 mL erlenmeyer flask containing 10 mL water. The sample was slaked and dispersed with water; 25 mL of sucrose solution was added, and the flask was allowed to stand for 15 min with swirling at 5 min intervals. Calcium hydroxide

reacts with sucrose to form calcium sucrate and the released OH^- was titrated against 1 M HCl using a digital pH meter.

3.9 Calcium Carbonate Equivalency

1.0 g of NVS sample was placed in a 60 mL erlenmeyer flask. After adding 25 mL of 1.0 M HCl, the flask was heated to boiling for 5 min on a hot plate. The flask was cooled to room temperature, and then the sample was titrated with 1.0 M NaOH to a pH of 7 (McLean, 1982).

3.10 Total Organic Carbon

3.10.1 NVS Extracts

Total organic carbon (TOC) in the NVS extracts was determined with a TOC analyzer (C-190 Total Organic Carbon Analyzer, Rosemount Dohrmann). The NVS extracts were diluted 10 times and injected directly into the analyzer.

3.10.2 NVS Samples

TOC of the NVS samples was determined by subtracting total carbonate contents from total C contents (Nelson and Sommers, 1982). The total C content in NVS was measured by dry combustion using an oven at 950 °C. Total inorganic C was determined by measuring the volume of CO_2 generated by adding 6M HCl- FeCl_2 solution to the sample.

3.11 Ammonia

After adjusting the pH to around 9.5 with 6M NaOH solution using a pH meter, 25 mL of the extract was placed into the Kjeldahl flask. The flask was connected to a steam-out distillation apparatus. Approximately 40 mL distillate was collected in a 60 mL erlenmeyer flask containing 10 mL of boric acid solution. Total NH_3 was determined by titrating the distillate with standard H_2SO_4 until the indicator turned a pale lavender (original color of boric acid indicating solution) (APHA-AWWA-WEF, 1995).

3.12 Total Organic Nitrogen

Total organic nitrogen (TON) was determined by the total Kjeldahl nitrogen (TKN) method using the residue from the NH_3 analysis (APHA-AWWA-WEF, 1995). Since TKN is the sum of organic N and NH_3 , the procedure using NH_3 -free residue gives organic N content only. A digestion reagent (H_2SO_4 with K_2SO_4 and CuSO_4) was carefully added to a distillation flask containing the NVS or NVS extract. The flask was placed in a block digester and heated under a hood until copious white fumes were observed. After 30 minutes heating, the sample was cooled to room temperature and diluted with 50 mL water. Then, 30 mL of sodium hydroxide-thiosulfate reagent was carefully added, and the flask was connected to a steam-out distillation apparatus. 40 mL of distillate was collected in a 60 mL erlenmyer flask containing 20 mL of boric acid solution. TON was determined by titration as described in NH_3 analysis (section 3.11).

3.13 Nitrate, Sulfate, and Chloride

Concentrations of NO_3^- , SO_4^{2-} , and Cl^- were determined by ion chromatography (DIONEX 2000I, DIONEX, Sunnyvale, CA) (APHA-AWWA-WEF, 1995). The NVS extract was filtered through a C-18 column before injection.

3.14 Carbonate and Bicarbonate

Concentrations of carbonate and bicarbonate were assumed to be equivalent to the inorganic C measured by the TOC Analyzer (Rosemount Dohrmann, C-190 Total Organic Carbon Analyzer).

3.15 Phosphate

Phosphate concentration was determined by the vanadomolybdophosphoric acid colorimetric method (APHA-AWWA-WEF, 1995). In this procedure, 35 mL of NVS extract was placed in a 50 mL volumetric flask. Then, 10 mL of vanadate-molybdate solution was added and brought to 50 mL with distilled water. After 10 min, the absorbance was measured at a wavelength of 420 nm.

3.16 Protein

Total protein concentration in the NVS extract was determined by the modified Lowry procedure (Raunkjær et al., 1994; Herbert et al., 1971) using a Micro Protein Determination Kit (Sigma, 1991) in which 2.2 mL of a Biuret reagent was added to

0.2 mL diluted sample in a test tube. After mixing, the tube was allowed to stand at room temperature for 10 min. Then, 0.1 mL of Folin and Ciocalteu's Phenol reagent was added to the tube, and the sample was mixed immediately. After 30 min, the samples were transferred to cuvetts and the absorbance was measured at 725 nm in a spectrophotometer. The total protein concentrations were determined from a calibration curve obtained by using protein standard, bovine albumin in NaCl solution.

3.17 Amino Acid

Individual amino acid concentration was determined with an amino acid analyzer (Model 476A Protein Sequencer System, Applied Biosystems). The NVS extracts sample was analyzed with and without hydrolysis. Unhydrolyzed sample analysis gives only free amino acid concentrations. Analyzing hydrolyzed sample shows total concentration of free amino acids and proteins.

3.18 Carbohydrate

Total concentration of carbohydrates was analyzed by the Anthron Carbohydrate Method (Raunkjær et al., 1994) in which 1 mL of cold anthrone reagent was added to a Pyrex test tube containing 1 mL of NVS extract. The test tube was closed with a rubber stopper and immediately mixed. The tube was then placed in a water bath at 100°C for 14 min, and subsequently refrigerated in a water bath at 5°C for 5 min. The absorbance of the samples and standards was measured at 625 nm with a spectrophotometer.

3.19 Inductively Coupled Plasma Elemental Analysis

3.19.1 Digestion of Solid Samples

Approximately 0.5 g of solid sample (dry basis) was placed into digestion vessels and 5 mL of deionized water and 5 mL of 70% HNO₃ were added to the vessel. The vessels were placed in a microwave digester (Microwave Digestion System MDS 2100, CEM Co., Matthews, NC), and digested using the "SLUDGE" method, EN-7 (CEM Co., Matthews, NC).

3.19.2 Digestion of NVS Extracts

25 mL of NVS extract was transferred into a digestion vessel, and 10 mL of HNO₃ was added to each vessel. The sample was digested using the microwave digester with the "TCLP EXTRACT" method, EN-10 (CEM Co., Matthews, NC).

3.19.3 ICP Elemental Analysis

Total concentrations of macro and trace elements in NVSs and NVS extracts were measured by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) (Optima 3000, Perkin-Elmer Co., Norwalk, CT).

3.20 Fourier Transformation Spectroscopy

NVS extract was scanned with Fourier Transformation Infrared (FT-IR) spectroscopy (Mattson Instruments, Madison, WI). The sample was prepared by adjusting the pH to 5-9 before placing in the liquid cell.

3.21 Chemical Speciation Calculation

Chemical speciation of the NVS extracts was determined with the geological speciation model Phreeqc 1.6 using the MINTEQ database to predict equilibrium distributions of major chemical species. MINEQL+ was used to predict interactions between trace metals and amino acids.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 XRD of Alkaline Reagents and NVS

X-ray diffraction (XRD) was performed on four alkaline reagents, FBA, LKD, FA, and CKD, and on the two types of NVSs. Major components of these materials are summarized in Tables 4.1 and 4.2.

4.1.1 Fluidized Bed Ash

FBA is one of the mineral residuals generated during burning of coal for electricity generation, and is usually collected from modern fluidized bed burners. The chemical composition depends on the coal type. XRD indicated that anhydrite (CaSO_4) is a major component of FBA (Fig. 4.1). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was considered as another major compound in FBA (Logan, 1993), but it was not observed with XRD. In the sample preparation processes, the alkaline reagents were dried at 110°C for 24 hours. Therefore, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ could have lost H_2O and been converted

into CaSO_4 (Nelson et al., 1978). FBA also contained lime (CaO), quartz (SiO_2), hematite (Fe_2O_3), periclase (MgO), and calcite (CaCO_3).

4.1.2 Lime Kiln Dust

LKD is a byproduct of lime (CaO or MgO) production by calcining calcitic or dolomitic limestone, and therefore LKD contains large amounts of MgO and CaO (Fig. 4.2). XRD also indicated the presence of calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$], which are primary components of limestone.

4.1.3 Fly Ash

FA is collected from the smoke stacks of coal burning plants by bag houses, electrostatic precipitators, or in down washes. FA usually has high Si content, mostly in the form of spherical glasses. Quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), and hematite (Fe_2O_3) were detected with XRD (Fig. 4.3). Broad peaks around $20\text{-}30^\circ$ indicated the presence of large amounts of glasses (approximately 40%). Also, many other types of oxides, FeO , CaO , MgO , K_2O , and Na_2O , have been found in coal fly ash (Kirby and Rimstidt, 1993; Lichtman and Mroczkowski, 1985; Furuya et al. 1987). These minerals can immobilize many trace metals by adsorption on their large surface area.

Alkaline Reagents	Major Components	Relative abundance (%) ¹⁾
Michigan State Fluidized Bed Ash (FBA)	Anhydrite (CaSO ₄)	40
	Lime (CaO)	16
	Quartz (SiO ₂)	15
	Hematite (Fe ₂ O ₃)	11
	Periclase (MgO)	10
	Calcite (CaCO ₃)	8
Martin Marietta Lime Kiln Dust (LKD)	Periclase (MgO)	30
	Lime (CaO)	24
	Calcite (CaCO ₃)	23
	Dolomite [CaMg(CO ₃) ₂]	12
	Anhydrite (CaSO ₄)	11
Wyandotte, Michigan dead Fly Ash (FA)	Quartz (SiO ₂)	52
	Mullite (Al ₆ Si ₂ O ₁₃)	34
	Hematite (Fe ₂ O ₃)	14
Cement Kiln Dust (CKD)	Calcite (CaCO ₃)	41
	Lime (CaO)	24
	Quartz (SiO ₂)	15
	Anhydrite (CaSO ₄)	9
	Portlandite [Ca(OH) ₂]	6
	Dolomite [CaMg(CO ₃) ₂]	5

1) Relative abundance based on peak intensities of crystalline phases.

Table 4.1 Major mineral constituents of four alkaline reagents used in the N-Viro Processes.

4.1.4 Cement Kiln Dust

CKD is a byproduct of cement manufacture. This material is fine-grained and very dry. Also, CKD is effective in absorbing odors of biosolids because of its high

surface area. The mineral composition depends on the constituents of the limestone and clay used in cement manufacture. CKD contains CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$, the primary components of limestone, and also CaO and MgO produced from the calcination process (Fig. 4.4). CKD can also contain kaolinite, mica, vermiculite, or montmorillonite from clay; however, these minerals were not observed in XRD, probably because the concentrations were lower than the XRD detection limit.

Alkaline Reagents	Major Components	Relative abundance (%) ¹⁾
NVS1 (Toledo)	Calcite (CaCO_3)	23
	Anhydrite (CaSO_4) ²⁾	21
	Quartz (SiO_2)	19
	Dolomite [$\text{CaMg}(\text{CO}_3)_2$]	12
	Periclase (MgO)	10
	Hematite (Fe_2O_3)	8
	Portlandite [$\text{Ca}(\text{OH})_2$]	7
NVS2 (Anderson)	Calcite (CaCO_3)	56
	Quartz (SiO_2)	14
	Anhydrite (CaSO_4) ²⁾	10
	Portlandite [$\text{Ca}(\text{OH})_2$]	8
	Dolomite [$\text{CaMg}(\text{CO}_3)_2$]	7
	Lime (CaO)	5

1) Relative abundance based on peak intensities of crystalline phases.

2) Logan et al. (1993) reported the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in N-Viro Soil using XRD. However, there was no gypsum detected in this study. Probably, most of gypsum was converted to anhydrite (CaSO_4) during the drying process at 110 °C for 24 hrs.

Table 4.2 Major mineral constituents of NVSs.

Fig. 4.1 XRD patterns of Michigan State fluidized bed ash (FBA).

Fig. 4.2 XRD patterns of Martin Marietta lime kiln dust (LKD).

Fig. 4.3 XRD patterns of Wyandotte Michigan fly ash (FA).

Fig. 4.4 XRD patterns of cement kiln dust (CKD).

Fig. 4.5 XRD patterns of NVS1 (Toledo) fresh material.

Fig. 4.6 XRD patterns of NVS2 (Anderson) fresh material.

4.1.5 NVS

Calcite (CaCO_3), anhydrite (CaSO_4), and quartz (SiO_2) were the major components in both NVSs (Fig. 4.5 and 4.6). NVS1 had more Mg as periclase (MgO) because of the use of LKD at Toledo. Since NVS1 is made with coal ashes, it contains more CaSO_4 than NVS2 does. Higher CaO content in NVS2 was due to the use of CKD.

4.2 Solids Content

There was little change in solids content of NVSs through the period of analysis (Fig. 4.7). This tells us that there was no significant net movement of water in and out of the NVS piles during this study, although analysis of the soil below the piles showed some solute movement. NVS1 and NVS2 remained at 55-60 and 65-70 % solids contents (w/w), respectively. The difference in the solids content between the two NVSs is due to solids content in the original dewatered biosolids and the dose rates of the alkaline reagents (Table 3.2).

4.3 pH

pH is the most important factor that can affect the chemical characteristics of NVS. pH controls key reactions for many elements including adsorption-desorption, precipitation-dissolution, and complexation with organic matter.

Extracts of fresh NVSs had pHs >12, close to the equilibrium pH of $\text{Ca}(\text{OH})_2$. The NVS extract pH decreased with time to around 8 because $\text{Ca}(\text{OH})_2$ was converted

Fig. 4.7 Solids content changes in NVSs over twelve months.

Fig. 4.8 pH changes over time in NVS extracts.

into CaCO_3 through carbonation (Fig. 4.8). The NVS2 extracts maintained high pH for two months longer than that of NVS1 because of the higher Ca(OH)_2 content of NVS2, which is probably due to the use of CKD rather than coal ash in NVS2. The large standard deviations in 2-month old NVS1 and 4-month old NVS2 samples are due to the wide range of sample pH values (8-12) as the equilibrium rapidly shifted from that of Ca(OH)_2 to that of CaCO_3 .

4.4 Calcium Hydroxide

Fresh NVS2 had higher Ca(OH)_2 content than NVS1 (Fig. 4.9) because of the use of CKD in the biosolids stabilization process. Both Ca(OH)_2 contents gradually decreased with time, as they were carbonated. This explains the pH decrease (Fig. 4.8). XRD also showed change of Ca(OH)_2 contents (Fig. 4.11). In NVS1, Ca(OH)_2 peaks were gone after three months. There were Ca(OH)_2 peaks in fresh and 3-month old NVS2 samples, but the 6-month old sample had no XRD-detectable Ca(OH)_2 . pH in NVS extracts was totally correlated to Ca(OH)_2 content in the corresponding NVS samples (Fig. 4.10). As long as the Ca(OH)_2 content was higher than 2%, the pH remained around 12; however, as Ca(OH)_2 content decreased below 2%, the pH decreased rapidly to around 8.

Fig. 4.9 Ca(OH)_2 content changes over time in NVSs.

Fig. 4.10 Relationship between Ca(OH)_2 content in NVSs and pH in NVS extracts.

Fig. 4.11 XRD patterns of NVS1 (A) and NVS2 (B) at different times, 0, 3, 6 months. Peaks with arrows indicate portlandite [$\text{Ca}(\text{OH})_2$].

4.5 Electrical Conductivity

The higher electrical conductivity (EC) in NVS2 compared to NVS1 in the first four months corresponded to the higher Ca(OH)_2 content of NVS2 (Fig. 4.12). Conductivity decreased in both NVSs, similarly to the decrease in Ca(OH)_2 content because Ca(OH)_2 is more soluble than CaCO_3 . This suggests that Ca^{2+} and OH^- ions dominated the EC at the beginning.

After five months, EC in NVS1 extracts became higher than in NVS2 extracts due to differences in sulfate ion (SO_4^{2-}) concentrations in the extracts. Since NVS1 was made with coal ashes, it contained more CaSO_4 than NVS2. With time, as pH decreased, chemical equilibrium shifted to dissolution of CaSO_4 (section 4.9). Higher Mg concentration in the NVS1 after two months of storage (section 4.13.3) may also contribute the high EC in NVS1 extracts.

4.6 Total Organic Carbon

NVS1 had higher total organic carbon (TOC) (6-10% dry weight base) than NVS2 (3-5%) (Fig. 4.13). This difference is due to the solids content of the original dewatered biosolids (24% for Toledo versus 19% for Anderson). The alkaline dose rates were the same in both facilities; 50% dewatered biosolids and 50% alkaline reagents (Table 3.2). TOC decreased at the high pH condition because of leaching. After the pH reached an equilibrium value of 8, there was little change in TOC.

Fig. 4.12 Electrical conductivity (EC) changes over time in NVS extracts.

Fig 4.13 Total organic carbon (TOC) changes over time in NVSs.

Fig. 4.14 Dissolved organic carbon (DOC) changes over time in NVS extracts.

Initial dissolved organic carbon (DOC) was high in both NVS extracts, 2500 mg/L in NVS1 and 1200 mg/L in NVS2, as a result of the high initial pH (Fig 4.14). DOC decreased as pH decreased. The solubility of organic compounds is considerably influenced by pH because of their various functional groups such as carboxyl (-COOH) and hydroxyl (-OH). At high pH, these sites are negatively charged and the solubility of organic compounds increases. As pH decreases, solubility decreases as functional groups are protonated.

4.7 Nitrogen

4.7.1 Total Organic Nitrogen

TON decreased in both NVS1 and NVS2 over time, similar to the decrease in TOC (Fig. 4.15). NVS extracts had high organic N as well as organic C. Organic N concentrations decreased in both NVS extracts, similar to the decrease in DOC (Fig. 4.16). Major organic N sources are from proteins in the biosolids (section 4.12).

4.7.2 Carbon/Nitrogen ratio

The DOC concentration is proportional to the corresponding organic N concentration in the NVS extracts (Fig. 4.18). The slope of the straight line is 4.2. This tells us that the carbon/nitrogen (C/N) ratio in the NVS extracts was approximately 4 : 1 through the period of analysis, much lower than that of NVSs (range of the NVS1 C/N ratio: 10-13, range of the NVS2 C/N ratio: 8-12 (Fig. 4.17)).

Fig. 4.15 Total organic nitrogen (TON) changes over time in NVSs.

Fig. 4.16 Total organic nitrogen (TON) changes over time in NVS extracts.

Fig. 4.17 Carbon nitrogen ratio (C/N) changes over time in NVSs.

Fig. 4.18 Relationship between DOC and TON in NVS extracts.

This means that water soluble organic matter contains proportionally more N than does the solid phase organic matter. Proteins, a major organic N source (section 4.11), have high solubility under high pH. Also, the strong alkaline condition enhance hydrolysis of proteins to produce water-soluble amino acids.

4.7.3 Ammonia

Free NH_3 is highly toxic to fish if it is dissolved in water, and it also inhibits seed germination. Therefore, NH_3 is an environmental concern when utilizing products from biosolids as fertilizers. Most of the inorganic nitrogen in biosolids is in the form of ammonium (NH_4^+) rather than oxidized forms such as nitrate (NO_3^-) even though the wastewater is oxidatively treated. The equilibrium between NH_3 and NH_4^+ is pH dependent. While 99% of a NH_3 - NH_4^+ mixture is in the form of NH_4^+ at neutral pH or lower, at above pH 11, over 98% of the mixture is free NH_3 at equilibrium. Since fresh NVSs have pH around 12, NH_3 is considered to exist as free NH_3 .

Free NH_3 dropped rapidly with time (Fig. 4.19), due to the pH decrease and volatilization from the NVS piles. As pH decreased, NH_3 was converted into NH_4^+ and immobilized by actively growing microorganisms. NVS1 had very high initial NH_3 concentrations. In Toledo, anaerobically digested biosolids are treated with the N-Viro process, and a high percentage of the total N is converted into NH_3 during digestion.

Fig. 4.19 NH_3 concentration changes over time in NVS extracts.

Fig. 4.20 NO_3^- concentration changes over time in NVS extracts.

4.7.4 Nitrate

NO_3^- concentrations initially increased with time (Fig. 4.20), probably due to nitrification, the microbial conversion of NH_3 to NO_3^- (Eq. 4.3-4.4). A decline after five months was probably due to leaching because of the low capacity of NVSs to retain anions.

NVS2 had higher NO_3^- concentrations than NVS1. Whereas NVS1 lost most N as free NH_3 because of the combination of anaerobic digested biosolids and high initial pH, NVS2 retained organic N which was gradually converted into NO_3^- through proteolysis, aminization (Eq. 4.1), ammonification (Eq. 4.2), and nitrification (Eq. 4.3 and 4.4) (Pierzynski, 1994).

4.8 Sulfur

Both NVSs had high S contents, probably from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) in the alkaline reagents (Fig. 4.21). NVS1 had higher S contents

Fig. 4.21 Total S concentration changes over time in NVSs.

Fig. 4.22 SO_4^{2-} concentration changes over time in NVS extracts.

than NVS2 because of the use of coal ashes in Toledo. There was a significant loss of S (~10000 mg/kg) in NVS1 due to leaching of SO_4^{2-} . On the other hand, there was little change in the S content of NVS2.

Total S concentration increased corresponding to pH decrease in both NVS extracts (Fig. 4.22). Both NVSs had almost the same SO_4^{2-} concentrations and the same curves as those of total S concentration in NVS extracts. This means that almost all of the soluble S was in the form of SO_4^{2-} . The increasing SO_4^{2-} concentration can be explained by dissolution of CaSO_4 .

Both NVS extracts had high concentrations of Ca (Fig. 4.34) because of high solubility of $\text{Ca}(\text{OH})_2$ (Eq. 4.5), shifting the equilibrium toward precipitation of CaSO_4 (Eq. 4.7a). Ca concentration decreased as $\text{Ca}(\text{OH})_2$ was converted into CaCO_3 (Eq. 4.6) because the solubility of CaCO_3 is much lower than that of $\text{Ca}(\text{OH})_2$. With the significant decrease of Ca^{2+} concentration, equilibrium shifted to dissolution of CaSO_4 (Eq. 4.7b), and SO_4^{2-} was released.

$\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + 2 \text{OH}^-$	(Eq. 4.5)	Ca solubility is high
$\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	(Eq. 4.6)	Ca solubility decreases by carbonation
$\text{CaSO}_4 \leftarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	(Eq. 4.7a)	Equilibrium shifts to left at high Ca^{2+} concentration
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	(Eq. 4.7b)	Equilibrium shifts to right at low Ca^{2+} concentration, releasing SO_4^{2-} .

4.9 Phosphorus

P is well known as a primary nutrient for plant growth. Environmental concern about P is mostly related to eutrophication caused by large inputs of P into aquatic systems. The P in biosolids is considered to be a mixture of organic P and many types of phosphate salts. Generally, at high pH and high Ca concentrations, the initial condition of NVS, soluble P rapidly forms $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, which can be slowly converted to more stable forms such as $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, and various types of apatite $[\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2]$ (X: F, Cl, OH) (Pierzynski, 1994). The very low P extractability is controlled by the precipitation reactions. The total P contents of the materials were too low for identification of specific P minerals by XRD.

There was little change in P contents in both NVSs through the period of analysis (Fig. 4.23). This suggests that there was no significant movement of P out of the NVS piles. NVS1 had higher P contents (6000 mg/kg) than NVS2 (2000 mg/kg). NVS1 was made by anaerobically digested biosolids, and the decrease in volatile solids with digestion would have concentrated P. Also, because Toledo is in the Great Lakes Basin, the treatment plants practice P removal which results in greater P retention in the biosolids. Since most P in NVSs is from the biosolids, the concentration depends on the solids content of the biosolids and dose ratio of alkaline materials.

Fig. 4.23 Total P content changes over time in NVSs.

Fig. 4.24 Total P concentration changes over time in NVS extracts.

Fig. 4.25 PO_4^{3-} concentration changes over time in NVS extracts.

Fig. 4.26 Cl^- concentration changes over time in NVS extracts.

NVS extracts had very low total P concentration, < 5 mg/L (< 1 % of the NVS total P contents) (Fig. 4.24). Total P concentrations decreased with time, as a result of the decrease in DOC, suggesting that P was mostly associated with organic matter in the NVS extracts. On the other hand, orthophosphate concentrations increased with time (Fig. 4.25), probably due to dissolution of calcium phosphates and desorption from mineral surfaces.

Inorganic P mobility can be reduced by adsorption onto CaCO_3 (Doner and Lynn, 1989). First of all, phosphate adsorption may first occur at specific sites on calcite; then several types of calcium phosphates gradually crystallize, which leads to additional phosphate reaction (Griffin and Jurinak, 1973).

4.10 Chloride

Cl^- concentrations in both NVS extracts gradually decreased with time (Fig. 4.26) due to leaching. Solubilities of most metal halide salts (NaCl) are very high, and therefore Cl^- can be leached out of the NVS piles.

4.11 Protein and Amino Acid

Since NVS is made with municipal biosolids, there should be high levels of proteins. Both NVS extracts had high initial protein concentrations (2350 mg/L in NVS1, 1280 mg/L in NVS2) (Fig. 4.27), and they decreased with time exactly like the DOC concentration changes. The protein concentrations were proportional to both DOC and total organic N concentrations in the NVS extracts (Fig. 4.28 and 4.29).

Amino acid concentrations in the NVS extracts were measured with and without hydrolysis (Table. 4.3). Unhydrolyzed sample analysis gave only free amino acid concentrations. Analyzing the hydrolyzed sample showed total concentration of free amino acids and proteins. Using the amino acid analysis data for hydrolyzed samples, total C and total N concentrations (mg/L) were calculated. According to the calculated concentrations, C:N ratio would be 3.1-3.4 to 1. This indicates that proteins and amino acids contribute to the low C:N ratio (approximately 4.2) of NVS extracts (section 4.7.2). Proteins and free amino acids account for about 45% of total DOC and about 61% of TON (Fig. 4.32 and 4.33).

Fig. 4.27 Protein concentration changes over time in NVS extracts.

Fig. 4.28 Protein concentration against DOC concentration in NVS extracts.

Fig. 4.29 Protein concentration against TON concentration in NVS extracts.

Amino acids	NVS1		NVS2	
	aa ¹⁾	mmol/L aa+protein ²⁾	aa	aa+protein
Glycine (Gly)	229.9	2034.5	223.6	1378.0
Alanine (Ala)	441.7	3471.8	177.3	1779.7
Valine (Val)	112.6	2355.8	22.8	1116.0
Leucine (Leu)	105.3	2162.3	40.4	1055.3
Isoleucine (Ile)	64.4	1477.2	22.5	685.9
Serine (Ser)	287.8	847.0	173.6	509.8
Threonine (Thr)	63.7	659.7	48.1	390.8
Aspartate (Asp)	60.3	521.7	28.9	226.3
Glutamate (Glu)	89.0	890.0	49.9	483.4
Cysteine (Cys)	46.8	13.3	6.8	7.8
Metionine (Met)	32.0	442.5	11.1	64.2
Phenylalanine (Phe)	72.9	1002.7	38.6	416.1
Tyrosine (Tyr)	51.4	893.7	31.7	400.6
Lysine (Lys)	16.0	698.9	1.3	357.4
Arginine (Arg)	34.1	713.6	23.9	420.3
Histidine (His)	10.9	100.1	8.7	100.5
Proline (Pro)	90.2	1530.5	21.5	761.9

1) aa: free amino acid concentration determined by unhydrolyzed sample analysis.

2) aa + protein: free amino acid and protein concentration determined by hydrolyzed sample analysis

Table 4.3 Amino acid concentrations in fresh NVS extracts.

4.12 Carbohydrate

The total carbohydrate concentration in the NVS extracts decreased as the pH decreased, similarly to the DOC changes (Fig. 4.30). The concentration of carbohydrate was proportional to that of DOC (Fig. 4.31). Percentages of carbohydrate-C in DOC are 5.14 % in NVS1 and 3.35 % in NVS2 (Fig. 4.32). The difference in the carbohydrate proportion in DOC depends on the wastewater characteristics (Raunkjær et al., 1994).

4.13 Other Organic Compounds

4.13.1 Lipid, Fatty Acid, and Hydrocarbon

Lipids, long-chain fatty acids, and other hydrocarbon compounds were extracted from NVS extracts with n-hexane, methyl-tert-butyl ether, and chloroform (APHA-AWWA-WEF, 1995); however, none was detected. These compounds are very hydrophobic, and therefore they cannot be extracted by water. Low molecular weight fatty acids could be dissolved in the NVS extracts; however, the concentrations must have been lower than the detection limits (< 1%).

4.13.2 Humic Acid and Fulvic Acid

Humic acid (HA) and fulvic acid (FA) have been fractionated from many types of biosolids (Boyd and Sommers, 1990; Riffaldi et al., 1982; Boyd et al., 1980; Sposito et al. 1976). However, NVS extracts did not appear to contain HA or FA.

Fig. 4.30 Carbohydrate concentration changes over time in NVS extracts.

Fig. 4.31 Carbohydrate concentration against DOC concentration in NVS extracts.

Fig. 4.32 Percentage of proteins and carbohydrates in DOC in NVS extracts.

Fig. 4.33 Percentage of proteins in TON in NVS extracts.

There was no UV absorbance (280 nm) in the NVS extracts, indicating the absence of HA or FA in the NVS extracts. Lignin and melanin are considered as the main aromatic compounds to form HA and FA. Unlike yard waste or natural water, there is no lignin in municipal biosolids. Melanin and a few kinds of amino acids can be sources of HA and FA, but biosolids are probably low in these compounds.

4.13.3 Polymer

Conditioning polymers used in the wastewater treatment process could affect the organic composition of the NVS extracts because they are very water soluble. Polyacrylamine and positively charged polyamine are commonly used. These polymers contain N in their structure, and this might explain the low C:N ratio in the extracts (Fig. 4.18). However, according to mass balance calculations, the polymer percentage in total organic matter in the NVS extracts was too low. Also, functional groups of these polymers could not be detected by FT-IR.

4.14 Macro Elements

4.14.1 Calcium

NVS2 had higher Ca content than NVS1 because CKD contains more Ca than coal ashes (Fig. 4.34A). There was little change in total Ca concentration in the two NVSs through the period of analysis.

Both NVSs had high initial Ca extract concentrations because of high solubility of Ca(OH)_2 . The solubility of Ca(OH)_2 is much greater than that of CaCO_3

(Table 4.4), and therefore Ca concentration in the NVS extracts decreased with the conversion of Ca(OH)_2 to CaCO_3 (Fig. 4.34B).

Minerals	Chemical Formula	$\log K_{so}$ ¹⁾
Lime	CaO	32.80
Portlandite	Ca(OH)_2	22.68
Calcite	CaCO_3	- 8.47
Anhydrite	CaSO_4	- 4.64
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.85

1) K_{so} : solubility constant at 25 °C, 1 atm.

Table 4.4 Solubility constants of major calcium compounds.

Because of the relative abundance of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) in these materials, they controlled Ca solubility following carbonation.

At high Ca concentration, Mn, Fe(II), Co(II), or Cd can coprecipitate with CaCO_3 by adsorption (Sposito, 1989). The large amounts of CaCO_3 , CaSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and Ca^{2+} are believed to play important roles in limiting heavy metal leaching.

Fig. 4.34 Ca concentration changes in NVSs (A) and NVS extracts (B).

4.14.2 Potassium

NVS2 had higher K concentration than NVS1 (Fig. 4.35A) due to mica in the cement kiln dust (CKD). NVS2 extracts also had high K concentrations (Fig. 4.35B) resulting from dissolution of mica at high pH (Eq. 4.8). Muscovite and other potassium aluminosilicate minerals have relatively high solubilities. High K concentration in NVS2 significantly decreased after three months as pH decreased.

4.14.3 Magnesium

NVS1 had higher Mg content than NVS2 (Fig. 4.36A) because periclase (MgO) is the most abundant compound in LKD, which is used in the N-Viro process at Toledo. Mg concentrations in the NVS extracts increased as pH decreased, unlike other macro elements, Ca, K, and Na (Fig. 4.36B). According to XRD, fresh NVS1 had MgO peaks, but the 3-month old sample had no XRD-detectable MgO (Fig. 4.37). Mg concentration was correlated with SO_4^{2-} concentration (Fig. 4.38), indicating that the increase in Mg concentration may have resulted from the dissolution of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

Fig. 4.35 K concentration changes in NVSs (A) and NVS extracts (B)

Fig. 4.36 Mg concentration changes in NVSs (A) and NVS extracts (B).

Fig. 4.37 XRD patterns of NVS1 (Toledo) at different times, 0, 3, and 6 months, indicating disappearance of periclase (MgO).

Fig. 4.38 Mg concentration against SO₄²⁻ concentration in NVS extracts.

Minerals	Chemical Formula	$\log K_{so}^{1)}$
Periclase	MgO	21.51
Brucite	Mg(OH) ₂	16.79
Magnesite	MgCO ₃	- 8.03
Nesquehonite	MgCO ₃ ·3H ₂ O	- 5.62
Dolomite	CaMg(CO ₃)	-17.00
Epsomite	MgSO ₄ ·7H ₂ O	- 2.14
Artinite	MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O	9.60
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	-8.77

K_{so}: solubility constant (25 °C, 1 atm)

Table 4.5 Solubility constants of major magnesium compounds.

MgO can also easily take up water and CO₂ and be converted to a stable magnesium carbonate hydroxide compound, artinite [MgCO₃·Mg(OH)₂·3H₂O]. The solubility of this mineral is high (Table 4.5) and it is pH-dependent (Eq. 4.9). Thus, Mg concentration increases with pH drop.

4.14.4 Sodium

Na concentration in NVSs gradually decreased with time (Fig. 4.39A), probably due to leaching. Halite (NaCl), the dominant form of Na, is very water-soluble, and therefore could be leached. Both NVS extracts had relatively low Na concentrations compared with other macro elements, Ca, K, and Mg. Under high Ca^{2+} concentration, Na^+ can be easily exchanged. Therefore, the total Na concentration in NVS extracts decreased as Ca concentration decreased.

4.14.5 Summary

Fig 4.40 shows comparison of concentration changes in Ca, K, Mg, and Na in NVS extracts. As previously discussed, both NVS extracts had high initial Ca concentrations which decreased with the conversion from $\text{Ca}(\text{OH})_2$ to CaCO_3 . After carbonation, Ca concentrations were dominated by dissolution of CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ because the solubilities of these compounds are greater than that of CaCO_3 . Mg concentrations increased corresponding to the decrease in Ca concentrations in both NVS extracts. As CaO is converted to $\text{Ca}(\text{OH})_2$, MgO is readily transformed to brucite [$\text{Mg}(\text{OH})_2$] under atmospheric conditions. Since the solubility of $\text{Ca}(\text{OH})_2$ is greater than that of $\text{Mg}(\text{OH})_2$, Ca^{2+} and OH^- dominate the system and suppress the dissolution of $\text{Mg}(\text{OH})_2$ at the initial phases. After the carbonation of hydroxide compounds, sulfate compounds would dominate the system. The increase in Mg

Fig. 4.39 Na concentration changes in NVSs (A) and NVS extracts (B).

concentration is attributed to the dissolution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ because of the higher solubility of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ than CaSO_4 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This explains the decreased Ca concentration and increased Mg concentration.

Minerals	Chemical Formula	$\log K_{so}^{1)}$
Lime	CaO	32.80
Periclase	MgO	21.51
Portlandite	Ca(OH)_2	22.68
Brucite	Mg(OH)_2	16.79
Calcite	CaCO_3	- 8.47
Magnesite	MgCO_3	- 8.03
Nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	- 5.62
Anhydrite	CaSO_4	- 4.64
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.85
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	- 2.14

K_{so} : solubility constant (25 °C, 1 atm)

Table 4.6 Comparison of solubility constants among Ca and Mg compounds.

Fig. 4.40 Comparison of concentrations (mmol/L) of macro elements, Ca, K, Mg, and Na in NVS1 extracts (A) and NVS2 extracts (B).

4.15 Oxide-Forming Elements

4.15.1 Aluminum

NVS1 had higher Al contents than NVS2 because coal fly ash, one of the alkaline reagents used for the biosolids stabilization in Toledo, contains mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and many other aluminosilicate compounds (Fig. 4.41). There was little Al in either NVS extract.

4.15.2 Iron

Higher Fe contents in NVS1 is probably due to hematite (Fe_2O_3) and magnetite (Fe_3O_4) in coal ashes and the use of FeCl_2 for P removal (Fig. 4.42). In Toledo, FeCl_2 is required to precipitate phosphate in wastewater treatment processes. Fe concentrations in NVS extracts were very low (< 0.3 mg/L). Slightly higher Fe concentration in NVS1 over the first 4 months was probably due to the FeCl_2 usage.

4.15.3 Manganese

NVS2 had higher Mn content than NVS1 (Fig. 4.43). MnO_2 is the most stable form of Mn. As well as Al and Fe, trace amounts of Mn were extractable.

Fig. 4.41 Al concentration changes in NVSs (A) and NVS extracts (B).

Fig. 4.42 Fe concentration changes in NVSs (A) and NVS extracts (B).

Fig. 4.43 Mn concentration changes in NVSs (A) and NVS extracts (B).

4.15.4 Summary

Both NVSs had high contents of Al, Fe, and Mn, and there was very little change in concentration in one year in the field (Table 4.7). These three elements are considered to exist as oxides and hydroxides, and have high sorption capacities for trace elements.

	Al	Fe	Mn
	mg/kg $\pm$ std.dev. ¹⁾		
NVS1	41300 $\pm$ 1000	38400 $\pm$ 1500	343 $\pm$ 6.9
NVS2	26500 $\pm$ 610	16500 $\pm$ 330	986 $\pm$ 17

1) std.dev.: standard deviation

Table 4.7 Average concentrations (mg/kg) of Al, Fe, and Mn in 40 NVS samples over twelve months.

Trace element adsorption on oxides and hydroxides of Al, Fe, and Mn has been studied by many researchers (Elliott et al., 1986; Hsu, 1989; Schwertmann and Taylor, 1989, and McKenzie, 1989). There is a typical affinity sequence of trace elements for adsorption on Al, Fe, and Mn oxides or hydroxides (Table 4.8). The oxides and hydroxides of these three elements provide similar types of adsorptive sites for the trace elements with terminal and bridging OH⁻ bound to a metal ion, usually Fe³⁺, Al³⁺, or Mn^{3+, 4+}. Generally, while Pb and Cu are tightly adsorbed on Fe and Al oxides and silica, Mn oxides have high affinity for Pb, Cu, Mn, and, Co.

Oxides or Hydroxides	Cationic Trace Element Adsorption
Al ¹⁾	Cu > Pb > Zn > Ni > Co > Cd
Fe ²⁾	Cu > Pb > Zn > Cd > Co > Ni > Mn
Mn ³⁾	Pb > Cu > Mn > Co > Zn > Ni

1) Hsu, 1989; 2) Schwertmann and Taylor, 1989; 3) McKenzie, 1989

Table 4.8 Trace element adsorption on Al, Fe, and Mn oxides and hydroxides.

4.16 Trace Elements

Trace element extractability is influenced by complicated reactions including dissolution-precipitation, adsorption-desorption, and complexation with organic matter. This section discusses trace element behavior in NVSs, considering concentration changes with time. The trace elements are categorized as metals and ligands (oxyanions).

4.16.1 Cationic Trace Elements (Metals)

4.16.1.1 Barium

NVS1 had higher Ba contents than NVS2. The Ba concentration in the NVS extracts decreased with time, corresponding to the pH change (Fig. 4.44). Generally, Ba is not very mobile because of precipitation with sulfate or carbonate and strong adsorption on clays such as vermiculites which have a high cation exchange selectivity for Ba²⁺.

Fig. 4.44 Ba concentration changes in NVSs (A) and NVS extracts (B).

4.16.1.2 Cadmium

NVS1 had a higher Cd concentration (6-8 mg/kg) than NVS2 (3-5 mg/kg) (Fig. 4.45), but there was no detectable Cd in either NVS extract. Cd is mobile in acidic soils because of weak adsorption on organic matter, clays, and oxides. However, above pH 7.0, Cd can be immobilized by coprecipitation with CaCO_3 (McBride, 1979; McBride, 1980) and precipitation as carbonate and phosphates. In the NVS pH range of 8 to 12, Cd mobility is limited, and therefore no Cd was detected in either extract.

4.16.1.3 Cobalt

Co concentration in NVSs ranged from 11-15 mg/kg (Fig. 4.46). Very little Co was extracted, and the concentration decreased with time. Generally, Co is mostly adsorbed and coprecipitated with Fe and Mn oxides. At high pH, Co mobility is limited by adsorption on Fe and Mn oxides and silicate clays, and probably by precipitation as the hydroxide, Co(OH)_2 . Also, Co mobility is related to organic matter. Relatively high initial Co concentration is probably correlated with initially high DOC concentrations of the NVS extracts.

Fig. 4.45 Cd concentration changes in NVSs.

Fig. 4.46 Co concentration changes in NVSs (A) and NVS extracts (B).

4.16.1.4 Chromium

Cr concentrations in NVS1 were high (200 mg/kg) compared with that in NVS2 (40 mg/kg) (Fig. 4.47). However, there was very little Cr in their extracts (less than 0.05 mg/L). Cr can take +6 oxidation state as chromate (CrO_4^{2-}), a very toxic form, under oxidizing conditions. In soils, however, Cr exists as +3 oxidation state as the Cr^{3+} (chromic) form. The mobility of Cr^{3+} is restricted by strong complexation with organic matter and adsorption on oxides and silicate clays. Furthermore, Cr^{3+} can easily substitute for Fe^{3+} in mineral structure, and precipitate as insoluble hydroxide form $[\text{Cr}(\text{OH})_3]$ at higher pH. Cr is a very immobile element, and therefore only trace amounts of Cr were extracted from NVSs even though NVSs had high Cr contents.

4.16.1.5 Copper

Cu is known to associate with organic compounds, and therefore the Cu concentration in NVS extracts decreased as DOC concentration decreased, corresponding to the pH drop (Fig. 4.48). Also, Cu is strongly adsorbed on oxides of Fe and Mn (hematite, goethite, birnessite), amorphous Fe and Al hydroxides, and clays (montmorillonite, vermiculite, imogolite). Above pH 6, Cu can precipitate as cupric hydroxide $[\text{Cu}(\text{OH})_2]$, oxide (CuO), or hydroxy-carbonates such as malachite $[\text{Cu}_2(\text{OH})_2\text{CO}_3]$ and azurite $[\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2]$. At high pH, Cu is immobilized by increased adsorption and precipitation. Thus, Cu solubility under strong alkaline conditions depend on complexation with organic matter. Cu has the higher affinity for organic matter than any other divalent transition metal, especially for selective

Fig. 4.47 Cr concentration changes in NVSs (A) and NVS extracts (B).

Fig. 4.48 Cu concentration changes in NVSs (A) and NVS extracts (B).

complexing groups (amines or polyphenols). At high pH, Cu can easily complex with proteins and amino acids, major organic compounds in NVSs, and they are readily extracted from NVSs at high pH. This can explain the proportional relationship between Cu and DOC.

4.16.1.6 Nickel

NVS1 had higher Ni contents than NVS2 because of coal ashes and LKD use in Toledo (Fig. 4.49). The Toledo sludge itself has had historically high Ni concentrations. The Ni concentration in the extracts corresponded to DOC concentration.

Ni is bound to organic matter very tightly, the second highest next to Cu among divalent transition metals. Since Ni has the smallest radius of the divalent transition metal cations, it can easily coprecipitate into octahedral sites of Mn and Fe oxides. Above pH 6, Ni favors adsorption on oxides, aluminosilicates, and clays. At high pH in NVSs, Ni mobility depends on DOC concentration.

4.16.1.7 Lead

Both NVSs had almost the same Pb contents (100-120 mg/kg) (Fig. 4.50). The extracted Pb concentration is very low (< 0.2 mg/L). The concentration corresponded to DOC concentration change. At high pH, Pb tends to form complexes with organic matter, adsorb on oxides and silicate clays, and precipitate as carbonate, hydroxide, or phosphate. Pb solubility in fly ashes and FGD byproduct is dominated by pH (Miller,

Fig. 4.49 Ni concentration changes in NVSs (A) and NVS extracts (B).

Fig. 4.50 Pb concentration changes in NVSs (A) and NVS extracts (B).

1995). Pb adsorption on soils is pH dependent and decreases as pH decreases from 8 to 3 (Harter, 1983; Elliott et al., 1986). In the NVS pH range of 8 to 12, however, almost all Pb is considered to be adsorbed on the mineral surface and unaffected by pH change.

4.16.1.8 Zinc

Both NVSs had relatively high Zn contents (500 mg/kg in NVS1, 200 mg/kg in NVS2), but there was little Zn in their extracts (Fig. 4.51). Generally, at higher pH, Zn solubility is limited by adsorption on oxides and aluminosilicates, and precipitation as Zn oxide, hydroxide, and hydrocarbonate. Complexation with organic matter and formation of Zn-hydroxy anions may increase Zn extractability. For sorption of Zn, Jurinak and Bauer (1956) reported the relative Zn adsorption on minerals as magnesite > dolomite > calcite. These carbonate compounds in NVSs may contribute for the low Zn mobility.

4.16.1.9 Others

Ag, Hg, and Tl were not detected in either NVS or in their extracts.

Fig. 4.51 Zn concentration changes in NVSs (A) and NVS extracts (B).

4.16.1.10 Summary of Trace Metals

High initial concentration of Cu in both extracts and Ni in NVS1 extract are attributed to their high affinity for DOC, especially to amine ligands. NVSs contain proteins and amino acids that provide many chelating sites for Cu and Ni. The high initial pH enhanced metal complexation and leaching of DOC and DOC-complexed metals. Cu and Ni concentrations decreased with time proportionally to DOC decrease and corresponding to the pH drop (Fig. 4.52 and 4.53). The difference in Ni concentrations in the two NVS extracts was attributed to the higher Ni content in NVS1 itself; 144 mg/kg in NVS1 and 36 mg/kg in NVS2. Co, Zn, Pb, and other trace metals seemed to be immobilized at high initial pH by adsorption on oxides and hydroxides of Al, Fe, and Mn and by precipitation as oxides, hydroxides, and carbonates. The chemical speciation calculation predicted that Zn and Pb precipitates as stable forms of oxides and hydroxides at high pH. Their low concentration did not change even though pH decreased from 12 to 8. The extractability of the trace metals was calculated by using the concentration of each element in NVSs and NVS extracts. The extractability changes are also correlated to DOC concentration changes (Fig. 4.54). The order of trace metal extractability in NVS was:

This corresponds to the Irving-Williams order for relative affinities of trace metals to organic matter. Consequently, trace metal extractability depends only on complexation with organic matter. Although NVSs had large pH drop, desorption from mineral surfaces or dissolution of salts did not seem to affect trace metal

mobility. To the contrary, once pH decreased to 8, trace metal extractability decreased, corresponding to decreased DOC concentration.

McBride (1998) and Richards et al. (1997) also reported high extractability of Cu and Ni in fresh NVS resulting from complexation with high DOC concentration at high pH (Table 4.9). Because of different sources of NVS and extraction methods, extractability in this study was slightly lower than their results, especially for Cu; 43-47 % Cu was extractable in their experiment, much higher than in NVS1 and NVS2. However, the order of extractability was the same: Cu > Ni > Co > Zn > Pb.

	NVS1	NVS2	McBride (1998) ¹⁾		Richards et al.
			N-Viro A ²⁾	N-Viro B ³⁾	(1997) ⁴⁾
Cu	23.1	22.7	47	45	42.9
Ni	18.9	9.4	24	15	24.2
Co	4.9	5.9	N/A ⁵⁾	N/A	11.2
Zn	0.9	2.1	0.6	0.4	ND ⁶⁾
Pb	0.8	0.6	< 0.1	< 0.1	N/A

1) Water extract samples

2) N-Viro A (McBride, 1998) was the same material used by Richards et al. (1997). Source: Syracuse, NY.

3) Source: Phillipsburg, NJ.

4) Toxicity characteristics leaching procedure (TCLP) Source: Syracuse, NY.

5) N/A: not available

6) ND: not detected

Table 4.9 Comparison of extractability (%) of Cu, Ni, Co, Zn, and Pb in fresh NVS materials (pH ≈ 12).

Fig. 4.52 Comparison of concentrations ($\mu\text{mol/L}$) of cations, Co, Cr, Cu, Ni, Pb, and Zn in NVS1 extracts (A) and NVS2 extracts (B)

Fig. 4.53 Relationship between dissolved organic carbon (DOC) concentrations and cations (Co, Cr, Cu, Ni, Pb, and Zn) concentrations in NVS1 extracts (A) and NVS2 extracts (B).

Fig. 4.54 Comparison of extractabilities of Co, Cu, Ni, Pb, and Zn in NVS1 extracts (A) and NVS2 extracts.

4.16.2 Anionic Trace Elements (Oxyanions)

4.16.2.1 Arsenic

As is a common constituent of coal, and therefore NVS1 had higher As content than NVS2 (Fig. 4.55). No As was detected in the extracts. As can have various oxidation states, as arsenite (+3) in the forms of As(OH)_3 , As(OH)_4^- , $\text{AsO}_2(\text{OH})^{2-}$, and AsO_3^{3-} and as arsenate (+5) in the form of AsO_4^{3-} . AsO_4^{3-} behaves like phosphate in soils; it is adsorbed on Fe and Al oxides, aluminosilicates, and silicate clay. The chemical behavior of As(OH)_3 resembles that of boric acid $[\text{B(OH)}_3]$ (section 4.16.2.2), forming the anion at high pH:

As(OH)_3 adsorption is most favorable at pH 7-9, similarly to B(OH)_3 . CaCO_3 and CaO application to soil immobilizes As as Ca arsenate precipitates. In NVS, As seems to be immobilized by adsorption on oxides and precipitation with Ca.

4.16.2.2 Boron

NVS1 had higher B content than NVS2 because of the use of coal ashes (Fig. 4.56). B concentration in the extracts increased as pH decreased.

At high pH, B forms borate $[\text{B(OH)}_4^-]$:

Fig. 4.55 As concentration changes in NVSs.

Fig. 4.56 B concentration changes in NVSs (A) and NVS extracts (B).

Adsorption of borate on Al and Fe oxides is most effective at pH 8-9 (Sposito, 1989). B concentration should have decreased as pH shifted from 12 to 8. Under high Ca concentration, however, B tends to precipitate as relatively insoluble Ca borate salts. Also, increased SO_4^{2-} could displace adsorbed borate from the mineral surface. Consequently, increased B concentration in NVS extracts with time is probably due to exchange with SO_4^{2-} , and possibly dissolution of Ca borate salts as CaCO_3 precipitated.

4.16.2.3 Molybdenum

Mo contents were 10-18 mg/kg in both NVS1 and NVS2 (Fig. 4.57). There was little Mo in the extracts (< 0.4 mg/L). Mo concentration in the NVS extracts increased slightly with time. MoO_4^{2-} is the major form of Mo in neutral to moderate by alkaline pH ranges. MoO_4^{2-} can be coprecipitated with CaCO_3 . Adsorption on Al, Fe, and Mn hydrous oxides is also favored at higher pH. Generally, application of phosphate to soils releases MoO_4^{2-} from bonding sites, and therefore introducing large amount of anions may have increased Mo concentration. The slightly increased Mo concentration in NVS extracts is probably due to exchange with increased SO_4^{2-} .

4.16.2.4 Selenium

Se forms oxyanions, selenites (SeO_3^{2-}) and selenates (SeO_4^{2-}); however, no Se was detected in either NVSs or their extracts.

Fig. 4.57 Mo concentration changes in NVSs (A) and NVS extracts (B).

4.16.2.5 Vanadium

NVS1 had high V contents (110-140 mg/kg) (Fig. 4.58), but there was no detectable V in the extracts in both NVSs. V can have various oxidation states as anionic forms ($\text{VO}_3(\text{OH})^{2-}$, $\text{VO}_2(\text{OH})_2^-$, $\text{VO}(\text{OH})_3^0$) and as the cations, VO^{2+} and V^{3+} . The anions behave like phosphate and many other oxyanions, and therefore adsorb on oxides and silicates. The cations bond to organic matter very tightly and adsorb on oxides and aluminosilicates. Also, V can replace Fe, Ti, and Al in crystal structures.

4.16.2.6 Summary of Oxyanions

Most oxyanion concentrations were very low in NVS extracts. Their extractabilities must have been suppressed by adsorption on mineral surfaces such as Al, Fe, and Mn oxides and possibly on calcite surfaces. Only B and Mo extractabilities were relatively high, and tended to increase with time. As mentioned previously, the increasing extractability probably resulted from exchange with increased SO_4^{2-} . SO_4^{2-} could displace borate from adsorption sites. The dissolution of Ca borate compounds may also have increased B concentration.

At the high initial pH and high Ca concentrations, precipitation reactions are favored. With pH drop and decreased Ca concentration, the equilibrium shifts to dissolution of Ca borate compounds (Eq. 4.12 and 4.13). Increasing Mo extractability with time can

also be explained by exchange with SO_4^{2-} . Changes in extractabilities of B, and Mo were exactly correlated to that of S (Fig. 4.59).

Richards et al. (1997) reported high Mo extractability (50.3 %) with TCLP (Table 4.10). In the TCLP, a weak acetic acid is used as an extracting solution, and therefore the NVS materials could be neutralized, and MoO_4^{2-} could be released. In addition, since the TCLP is used as an empirical index of short-term mobility, these results cannot be compared directly.

	NVS1	NVS2	McBride (1998) ¹⁾		Richards et al.
			N-Viro A ²⁾	N-Viro B ³⁾	(1997) ⁴⁾
Mo	4.1 (11.7) ⁵⁾	8.3 (16.9)	13	11	50.3

1) Water extract samples

2) N-Viro A (McBride, 1998) was the same material used by Richards et al. (1997).
Source: Syracuse, NY.

3) Source: Phillipsburg, NJ.

4) Toxicity characteristics leaching procedure (TCLP) Source: Syracuse, NY.

5) Numbers in parentheses indicate maximum extractability (5-month old sample of NVS1 and at 6-month old sample of NVS2).

Table 4.10 Comparison of extractability (%) of Mo in fresh NVS materials.

Fig. 4.58 V concentration changes in NVSs.

Fig. 4.59 Comparison of extractabilities of S, B, and Mo in NVS1 extracts (A) and NVS2 extracts (B).

4.17 Soil Analysis

Significance of treatment and depth was examined with analysis of variance (ANOVA) using F-value and P-value (Table 4.11).

4.17.1 pH and EC

The surface soil (0-30 cm) pHs were relatively low (pH = 5-6) in both NVS underlying soils compared to the control (pH = 7) (Fig. 4.60). The soil pH was unaffected by the pile below 30 cm. At the beginning, the surface soil must have had high pH because of the NVS's high alkalinity. The electrical conductivity (EC) of the soils was much higher under the piles than that of the control in both soils (Fig. 4.61), and particularly so in soils under NVS1. Both surface soils had much higher S contents than controls as well (Fig. 4.62). S contents in the soil samples are almost proportional to the corresponding EC (Fig. 4.63). This indicates that the high EC in the surface soils was due to S leaching, in the form of SO_4^{2-} generated from dissolution of CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The much higher soil EC under NVS1 resulted from higher concentration of SO_4^{2-} than NVS2. The low soil pH was probably due to nitrification and organic acids leaching.

Dependent Variable	Independent Variable						
	Treatment		Depth		Treatment x Depth		F critical value*
	F	P	F	P	F	P	
pH	134.28	0.000	29.88	0.000	17.63	0.000	2.25
EC	1499.30	0.000	246.95	0.000	109.80	0.000	2.74
Al	8.60	0.000	139.48	0.000	2.56	0.024	2.17
B	0.12	0.887	165.54	0.000	3.68	0.004	2.25
Ba	16.93	0.000	49.97	0.000	11.08	0.000	2.25
Ca	8.42	0.001	5.91	0.002	38.35	0.000	2.25
Co	3.48	0.046	1.77	0.177	1.69	0.164	2.47
Cu	14.66	0.000	145.43	0.000	6.93	0.000	2.51
Fe	1.98	0.144	98.03	0.000	2.26	0.044	2.17
K	5.56	0.010	84.28	0.000	3.09	0.021	2.49
Mg	33.80	0.000	98.41	0.000	3.31	0.005	2.17
Mn	1.48	0.238	136.19	0.000	3.97	0.002	2.25
Na	41.90	0.000	46.76	0.000	4.54	0.001	2.25
Ni	12.96	0.000	125.52	0.000	4.12	0.007	2.60
P	1.24	0.314	90.76	0.000	0.70	0.656	2.66
S	613.11	0.000	92.57	0.000	63.36	0.000	2.42
V	3.06	0.064	56.13	0.000	0.95	0.477	2.47
Zn	3.86	0.038	62.81	0.000	1.31	0.297	2.60

*F critical value was obtained from Table X (a) F distribution critical values for tests with significance level .05 (Devore and Peck, 1993).

Table 4.11 Analysis of variance (ANOVA) on treatment and depth on soil sample analysis.

Fig. 4.60 Soil pH under NVS piles.

Fig. 4.61 Electrical Conductivity (EC) of soils under NVS piles

Fig. 4.62 Total sulfur (S) concentrations in soils under NVS piles

Fig. 4.63 Relationship between EC and total S concentration in soils under NVS piles

4.17.2 Elemental Analysis

Ca concentration in surface soil (0-5 cm) was very high under NVS1, more than 1500 mg/kg higher than control (Fig. 4.67). Although fresh NVS2 initially had higher soluble $\text{Ca}(\text{OH})_2$ content, the Ca concentrations in the soils were close to the control values. This implies that Ca leachate is attributed to dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ rather than $\text{Ca}(\text{OH})_2$ for a long term. There was no significant change in Ca concentration in below 5 cm in either soil. Slightly higher concentrations showed in Mg and Na in NVS1 (Fig. 4.72 and 4.74) and K in NVS2 underlying soils (Fig. 4.71), but P concentration was unaffected (Fig. 4.76). Surface soils (0-5 cm) had relatively high Cu and Ni concentrations (Fig. 4.69 and 4.75) because of their high extractability under high initial pH and DOC concentration. Ni concentration was higher in the surface soil (0-15 cm) under NVS1 than NVS2 because of the difference in total Ni concentration of NVSs (Fig. 4.49). There was no significant change in other trace metal concentrations; trace metal leaching is suppressed by adsorption and coprecipitation. Ag, Cd, Cr, Hg, Mo, Pb, and Tl were below detection limit in all soil samples.

Fig. 4.64 Al concentration in NVS underlying soils.

Fig. 4.65 B concentration in NVS underlying soils.

Fig. 4.66 Ba concentration in NVS underlying soils.

Fig. 4.67 Ca concentration in NVS underlying soils.

Fig. 4.68 Co concentration in NVS underlying soils.

Fig. 4.69 Cu concentration in NVS underlying soils.

Fig. 4.70 Fe concentration in NVS underlying soils.

Fig. 4.71 K concentration in NVS underlying soils.

Fig. 4.72 Mg concentration in NVS underlying soils.

Fig. 4.73 Mn concentration in NVS underlying soils.

Fig. 4.74 Na concentration in NVS underlying soils.

Fig. 4.75 Ni concentration in NVS underlying soils.

Fig. 4.76 P concentration in NVS underlying soils.

Fig. 4.77 S concentration in NVS underlying soils.

Fig. 4.78 V concentration in NVS underlying soils.

Fig. 4.79 Zn concentration in NVS underlying soils.

CHAPTER 5

CONCLUSIONS

Fresh NVS extracts had pHs >12 because of the presence of Ca(OH)_2 , but pH decreased to an equilibrium value of 8 with time, by conversion of Ca(OH)_2 to CaCO_3 . Field storage encourages carbonation of the Ca(OH)_2 . NVS2 extracts maintained high pH for three months longer than that of NVS1 because of the higher Ca(OH)_2 content of NVS2, which is due to the use of CKD rather than coal ashes. The pH was exactly correlated to total content of Ca(OH)_2 . Solubility, adsorption, and complexation with organic matter are greatly affected by pH. The pH change from 12 to 8 in NVS with field storage had a large impact on NVS chemical characteristics.

Conversion of Ca(OH)_2 to CaCO_3 greatly influenced Ca solubility. The solubility of Ca(OH)_2 is much greater than that of CaCO_3 , and therefore NVS had high initial Ca concentrations, which decreased with time. This Ca concentration change also affected the solubility equilibria of CaSO_4 . With the significant decrease in Ca^{2+} concentration, equilibrium shifted to dissolution of CaSO_4 , and SO_4^{2-} was released. Sulfate leaching affected underlying soil properties, especially in EC and S

concentration. High concentration of Ca seemed to be accumulated on the surface soil, especially under NVS1 that had higher gypsum content.

Because of NVS's high initial pH, ammonia exists as free NH_3 . While NH_3 can contribute to pathogen destruction in the N-Viro process, it can also limit seed germination when it is applied in the field. The NH_3 concentration was very high in NVS1. Because anaerobically digested biosolids are processed in Toledo, a high percentage of the total N is converted into NH_3 during digestion. With field storage, however, free NH_3 in NVS extracts dropped rapidly, probably due to the pH decrease and volatilization from the piles. While NVS1 lost large amounts of N in the N-Viro process and with field storage, NVS2 retained more organic N than NVS1 and provided higher NO_3^- concentration.

Since NVS is made with municipal wastewater residuals, it has a high level of organic matter containing proteins, carbohydrates, and lipids. Initial DOC was high in both NVS extracts as a result of high initial pH. With a pH decrease, DOC concentration decreased as well. Both NVS extracts had high organic N contents, approximately 4:1 in C/N ratio, probably due to water-soluble proteins and amino acids. Large amounts of DOC could affect trace element extractability, especially Cu and Ni which have high affinity for organic matter. The organic matter is also an energy source for microorganisms. These compounds could stimulate microbial activity, and possibly encourage plant growth.

NVS's unique properties, very high initial pH, high DOC concentration, large pH drop from 12 to 8, many Ca compounds, many metal oxides and hydroxides, and

release of SO_4^{2-} , resulted in uncommon trace element behavior. High initial pH immobilizes most trace metals by adsorption on oxides and hydroxides of Al, Fe, and Mn, precipitation as oxides, hydroxides, and carbonates, and coprecipitation with many Ca compounds such as CaCO_3 , CaSO_4 , CaHPO_4 , $\text{CaMg}(\text{CO}_3)_2$. Generally, these trace metals are released as pH decreases; however, concentrations of most trace metals in NVS extracts tended to decrease with pH drop. This result indicates that trace metal extractability depends on DOC concentration. Because of the very high DOC concentrations in NVS extracts, mostly from proteins and amino acids, metal-organic complexes were favored and they were leached because of their high water solubility; this was especially the case of Cu and Ni which have high affinity for organic matter, particularly to amine groups. Since DOC concentration decreased as pH decreased with time, Cu and Ni concentrations also decreased. Because of the high initial extractabilities of Cu and Ni, the underlying surface soil had relatively high concentration of these elements. Other trace metals also tended to decrease with time, even though the concentrations were very low. Generally, anion adsorption is most effective under pH 9, and therefore, anion concentrations should have decreased as pH decreased. However, most anions in NVS extracts tended to increase with pH drop from 12 to 8. This tendency must be associated with SO_4^{2-} generated from gypsum. High concentration of SO_4^{2-} can displace most oxyanions and inorganic anions from adsorption sites. Overall, extractability of trace elements was very low because of 1) coprecipitation with many Ca compounds, 2) adsorption on oxides on Al, Fe, and Mn, and silicate clays, and 3) precipitation as oxide, hydroxides, and

carbonates. Initial extractability of Cu and Ni was relatively high because of high affinity for organic matter. For oxyanions, the B concentrations tend to increase with time.

Odor is one of the public concerns in biosolids use. NVS2 is made with raw primary and activated biosolids, and therefore the fresh materials smelled like sludge. On the other hand, there was no bad odor in NVS1 because it is produced with aerobically digested biosolids. However, the anaerobic digestion reduces N concentration at the same time. The N loss in the material is a negative factor when using NVS as a fertilizer. As a soil amendment, fresh NVS had too high pH and EC for plant growth. High concentration of NH_3 could prevent germination of seeds. However, field storage improved NVS chemical characteristics by shifting the pH from 12 to 8, diminishing EC, and dispersing free NH_3 . NVS has been commonly used as an agricultural limestone substitute because of its high $\text{Ca}(\text{OH})_2$ and CaCO_3 contents. Gypsum has been used as a soil amendment to fertilize various soils, especially S-deficient soils. With its high content of S, NVS1 can be used as a gypsum substitute. This study showed dissolution of CaSO_4 and SO_4^{2-} leaching into the ground. NVS can be used for land reclamation, especially acidic minespoil or mine tailings, because of its acid neutralizing capacity, organic matter and nutrient contents, and soil-like physical properties. Particularly, high organic matter and nutrient contents can stimulate microbial activity and enhance reclamation.

Trace metal leaching is an environmental concern in biosolids application. This study proved that there was no significant change in trace metal concentration in the underlying soils.

This study shows that NVS can be safely used as a fertilizer, a soil amendment, a lime substitute, and a soil ingredient that provides many beneficial effects.

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APPENDIX

A. Numerical Data of Analysis

month	NVS1		NVS2	
	mean (%)	std. dev.	mean (%)	std. dev.
0	58.70	0.38	69.62	1.01
0.5	57.64	0.81	66.91	0.96
1	59.18	0.56	66.73	1.08
2	58.20	0.59	64.23	0.71
3	58.79	1.82	65.41	4.12
4	60.05	0.43	68.56	1.58
5	58.31	1.43	64.78	1.22
6	59.08	3.97	62.09	1.10
8	56.39	1.17	61.93	0.80
10	57.75	1.60	65.55	0.78
12	58.51	0.91	69.00	1.02

Table A.1 Solids content changes in NVSs (Fig. 4.7).

month	NVS1		NVS2	
	mean	std. dev.	mean	std. dev.
0	12.07	0.02	12.66	0.04
0.5	12.16	0.02	12.57	0.08
1	11.52	0.02	12.18	0.04
2	9.47	1.67	12.48	0.03
3	8.19	0.04	11.97	0.13
4	8.09	0.09	11.18	2.02
5	8.11	0.05	7.85	0.03
6	8.14	0.06	7.71	0.16
8	8.16	0.17	7.77	0.23
10	8.14	0.02	7.64	0.17
12	7.52	0.17	7.49	0.05

Table A.2 pH changes in NVS extracts (Fig. 4.8).

month	NVS1		NVS2	
	mean (%)	std. dev.	mean (%)	std. dev.
0	5.61	0.29	10.79	0.44
0.5	4.47	0.16	9.98	0.49
1	2.64	0.27	9.50	0.50
2	0.92	0.82	8.70	0.78
3	0.66	0.06	8.06	0.82
4	0.48	0.10	6.32	2.24
5	0.33	0.39	0.87	0.36
6	0.43	0.02	0.38	0.12
8				
10				
12				

Table A.3 Calcium hydroxide content changes in NVSs (Fig. 4.9).

month	NVS1		NVS2	
	mean (dS/m)	std. dev.	mean (dS/m)	std. dev.
0	10.33	0.12	12.63	0.29
0.5	9.80	0.20	11.57	0.51
1	9.05	0.42	11.27	0.06
2	6.44	1.18	10.73	0.21
3	5.76	0.26	10.04	1.03
4	6.19	0.48	8.70	2.87
5	6.08	0.52	4.25	0.40
6	4.70	0.81	3.86	0.11
8	3.91	0.35	3.03	0.20
10	3.98	0.29	3.11	0.24
12	4.67	0.41	3.45	0.29

Table A.4 EC changes with time in NVS extracts (Fig. 4.12).

month	NVS1		NVS2	
	mean (%)	std. dev.	mean (%)	std. dev.
0	9.19	0.11	3.13	0.13
0.5	9.81	0.26	4.14	0.58
1	8.97	0.12	4.78	0.30
2	7.41	0.09	4.55	0.08
3	7.71	0.72	4.81	0.40
4	7.03	0.06	3.92	0.30
5	7.21	0.20	2.54	0.64
6	6.97	0.37	3.03	0.11
8	6.53	0.03	3.21	0.02
10	6.75	0.11	2.76	0.37
12	6.12	0.03	2.75	0.03

Table A.5 TOC changes in NVSs (Fig. 4.13).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	2469.67	93.15	1251.67	69.41
0.5	1905.33	207.11	1462.67	156.29
1	1418.33	201.62	1572.33	92.00
2	386.06	141.50	1597.67	47.44
3	173.07	143.02	1174.23	519.58
4	173.50	67.66	670.52	377.81
5	140.86	64.32	108.23	35.79
6	96.63	26.83	98.59	30.85
8	46.07	6.93	50.00	8.81
10	37.14	0.29	48.01	12.28
12	66.36	3.21	67.01	4.15

Table A.6 DOC changes in NVS extracts (Fig. 4.14).

month	NVS1		NVS2	
	mean (mg/kg)	std. dev.	mean (mg/kg)	std. dev.
0	8967.92	344.38	4401.73	143.28
0.5	8376.55	265.50	5328.25	103.15
1	7802.26	604.32	5014.65	36.16
2	5908.30	51.43	5297.43	274.58
3	5656.36	122.95	4474.95	546.83
4	5662.35	109.63	3795.27	33.91
5	5724.00	257.21	3786.99	48.34
6	5194.89	728.07	4079.67	156.22
8	5846.69	185.57	3173.55	77.93
10	5677.56	137.68	3854.05	235.33
12	5940.31	32.97	3445.58	26.78

Table A.7 TON concentration in NVSs (Fig. 4.15).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	10.33	0.12	12.63	0.29
0.5	9.80	0.20	11.57	0.51
1	9.05	0.42	11.27	0.06
2	6.44	1.18	10.73	0.21
3	5.76	0.26	10.04	1.03
4	6.19	0.48	8.70	2.87
5	6.08	0.52	4.25	0.40
6	4.70	0.81	3.86	0.11
8	3.91	0.35	3.03	0.20
10	3.98	0.29	3.11	0.24
12	4.67	0.41	3.45	0.29

Table A.8 TON concentration in NVS extracts (Fig. 4.16).

month	NVS1		NVS2	
	mean	std. dev.	mean	std. dev.
0	10.76	0.09	6.98	0.24
0.5	11.85	0.24	7.72	0.95
1	11.22	0.71	9.51	0.52
2	12.58	0.10	8.76	0.27
3	13.53	1.17	11.31	1.77
4	12.33	0.14	10.29	0.69
5	12.81	0.34	6.67	1.42
6	13.71	1.73	7.32	0.19
8	11.05	0.28	10.04	0.15
10	11.99	0.17	7.04	1.00
12	10.29	0.07	8.00	0.06

Table A.9 C/N ratio changes with time in NVSs (Fig. 4.17).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	194.24	3.62	33.06	0.36
0.5	75.95	8.70	20.24	0.65
1	46.64	6.52	13.48	1.67
2	22.14	21.74	9.89	0.22
3	8.00	4.35	11.19	8.17
4	5.84	2.32	9.89	6.69
5	3.23	0.51	3.02	1.09
6	2.26	0.43	2.15	0.43
8				
10				
12				

Table A.10 Ammonia concentration changes in NVS extracts (Fig.4.19).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	1.36	1.44	0.43	0.09
0.5	1.02	1.18	0.41	0.11
1	0.53	0.33	0.61	0.27
2	7.83	4.35	0.55	0.16
3	6.46	1.67	1.73	2.00
4	12.76	1.58	7.50	2.40
5	16.25	1.77	55.26	17.96
6	12.87	2.14	39.70	11.29
8	11.04	0.00	30.92	0.00
10	6.56	0.00	15.75	0.00
12	5.28	0.00	23.19	0.00

Table A.11 Nitrate concentration changes in NVS extracts (Fig. 4.20).

month	NVS1		NVS2	
	mean(mg/kg)	std. dev.	mean(mg/kg)	std. dev.
0	47140.03	2393.43	20662.83	549.36
0.5	44019.22	2058.39	20733.40	1962.09
1	40302.85	1276.10	20574.18	1989.73
2	39447.82	1468.16	20939.57	1468.16
3	39391.04	1292.82	20492.67	1292.82
4	39002.49	1502.88	20814.63	1325.44
5	34585.99	549.36	19593.48	1363.20
6	34765.76	8.73	18988.56	659.66
8	33855.30	447.41	19666.89	1448.24
10	34882.68	659.66	18030.83	659.66
12	33730.13	1155.39	18416.66	549.36

Table A.12 Total S concentration changes in NVSs (Fig. 4.21).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	173.13	7.90	159.33	16.19
0.5	181.07	17.33	136.60	8.84
1	195.13	43.19	153.33	10.97
2	320.53	195.26	139.87	10.33
3	577.00	0.00	143.47	4.94
4	600.00	0.00	145.20	21.21
5	577.00	0.00	467.00	0.00
6	529.00	0.00	448.00	0.00
8	509.00	0.00	391.00	0.00
10	514.00	0.00	412.00	0.00
12	520.00	0.00	397.00	0.00

Table A.13 Sulfate concentration changes in NVS extracts (Fig. 4.22).

month	NVS1		NVS2	
	mean(mg/kg)	std. dev.	mean(mg/kg)	std. dev.
0	6091.19	28.86	2055.56	61.64
0.5	6184.75	89.49	2563.34	5.06
1	5998.56	68.00	2486.12	39.03
2	6159.03	142.14	2709.42	52.36
3	6064.44	99.14	2730.90	108.36
4	5812.24	48.87	2321.51	79.13
5	5739.80	150.59	2515.43	75.54
6	5890.22	98.38	2463.54	117.52
8	6004.23	97.30	2367.85	29.33
10	5840.26	128.74	2650.71	99.99
12	5825.96	10.10	2314.34	71.72

Table A.14 Total P concentration changes in NVSs (Fig. 4.23).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	5.01	3.6E-01	2.68	6.2E-03
0.5	3.77	4.6E-01	3.76	3.5E-01
1	2.55	5.0E-01	3.89	5.0E-02
2	2.43	1.3E-01	3.81	2.2E-01
3	1.91	1.0E-01	3.95	4.3E-02
4	1.38	1.2E-01	1.30	2.7E-01
5	1.53	1.1E-02	1.29	9.5E-02
6	0.86	2.3E-03	1.29	1.2E-02
8	0.77	3.8E-02	0.79	9.9E-03
10	1.29	5.8E-03	0.95	1.5E-02
12	0.86	3.6E-03	0.79	3.8E-02

Table A.15 Total P concentration changes in NVS extracts (Fig. 4.24).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	0.02	1.8E-02	0.01	1.2E-02
0.5	0.02	1.8E-02	0.02	1.7E-02
1	0.02	1.8E-02	0.01	1.2E-02
2	1.37	1.1E-01	0.01	1.2E-02
3	0.97	5.7E-02	0.01	1.4E-02
4	0.87	3.3E-02	0.01	1.4E-02
5	0.74	1.1E-01	0.13	4.0E-02
6	0.82	3.6E-02	0.21	5.0E-02
8	0.49	8.4E-02	0.21	6.5E-02
10	0.45	6.1E-02	0.22	4.6E-02
12	0.49	1.2E-01	0.20	5.5E-02

Table A.16 Phosphate concentration changes in NVS extracts (Fig. 4.25).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	556.50	31.82	563.50	21.92
0.5	463.50	82.73	544.50	27.58
1	470.00	14.14	704.00	16.97
2	420.00	73.54	682.00	14.14
3	429.00	38.18	712.00	0.00
4	334.50	103.94	544.00	79.20
5	274.00	93.34	420.00	101.82
6	146.00	42.43	376.00	45.25
8	68.33	18.77	176.00	14.14
10	54.67	23.12	130.00	14.14
12	42.33	16.07	75.00	4.24

Table A.17 Chloride concentration changes in NVS extracts (Fig. 4.26).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	2351.22	34.37	1283.17	32.90
0.5	1836.27	11.37	1168.11	15.69
1	1632.60	17.34	1271.18	57.70
2	536.23	34.62	1220.89	18.01
3	53.27	20.96	988.27	355.63
4	53.89	1.87	311.33	241.00
5	42.34	1.84	42.42	17.52
6	44.42	1.11	28.20	0.00
8				
10				
12				

Table A.18 Protein concentration changes in NVS extracts (Fig. 4.27).

month	NVS1		NVS2	
	mean (mg/L)	std. dev.	mean (mg/L)	std. dev.
0	10.33	0.12	12.63	0.29
0.5	9.80	0.20	11.57	0.51
1	9.05	0.42	11.27	0.06
2	6.44	1.18	10.73	0.21
3	5.76	0.26	10.04	1.03
4	6.19	0.48	8.70	2.87
5	6.08	0.52	4.25	0.40
6	4.70	0.81	3.86	0.11
8	3.91	0.35	3.03	0.20
10	3.98	0.29	3.11	0.24
12	4.67	0.41	3.45	0.29

Table A.19 Carbohydrate concentration changes in NVS extracts (Fig. 4.30)

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	178076.78	2922.89	314179.34	2211.34	1060.65	26.72	897.01	16.95
0.5	170761.75	2144.02	313850.88	2288.99	986.21	23.01	926.27	18.27
1	163901.92	896.63	313392.05	2260.29	645.77	9.85	916.29	17.75
2	172511.41	2195.98	309809.62	2147.44	313.07	0.55	908.87	17.79
3	170839.50	2171.32	312010.00	2263.76	337.68	2.05	888.65	16.96
4	167482.30	1530.94	311853.04	2163.13	356.61	1.33	649.91	9.08
5	166212.82	1602.17	301222.51	2098.16	348.57	1.22	461.73	3.89
6	163869.60	896.46	303233.30	2142.17	329.25	0.97	432.16	3.12
8	164716.88	1506.28	303964.29	2165.35	351.08	2.51	430.37	3.13
10	161580.54	1502.36	300762.86	2104.24	342.69	2.18	450.23	3.83
12	162810.10	890.66	298507.73	2079.25	322.25	12.43	428.50	0.50

Table A.20 Ca concentration changes in NVSs and NVS extrats (Fig. 4.34).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	9483.89	116.40	22326.79	86.40	102.37	1.06	441.01	0.91
0.5	9338.40	136.00	20566.28	127.30	86.47	1.79	470.04	1.06
1	9101.98	84.10	20501.97	61.60	93.35	0.65	430.38	1.29
2	8538.77	110.70	20543.59	57.40	86.47	1.07	441.41	1.13
3	8352.59	118.20	20080.47	74.30	89.41	0.52	375.79	1.23
4	8236.34	80.90	17431.15	108.90	81.65	1.03	213.90	0.99
5	8078.72	112.60	19191.49	103.40	72.68	1.08	200.89	0.97
6	8051.13	29.60	19140.12	89.30	35.61	1.13	186.96	0.62
8	8046.29	92.00	16926.60	74.30	30.39	0.56	159.18	2.38
10	7286.57	135.80	17562.87	42.40	33.88	0.85	144.29	1.95
12	7907.57	121.90	17140.86	77.40	30.24	0.67	144.15	2.17

Table A.21 K concentration changes in NVSs and NVS extrats (Fig. 4.35).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	43424.72	1570.30	15531.12	615.05	0.39	0.04	0.18	0.02
0.5	42858.05	1246.53	15772.71	876.51	0.52	0.04	0.13	0.01
1	42482.48	669.57	15948.65	602.55	6.40	0.54	0.20	0.03
2	40892.60	532.51	16077.10	636.45	421.60	57.53	0.26	0.04
3	39602.10	1005.18	15950.34	584.59	415.17	54.71	0.30	0.05
4	39843.56	965.30	15754.55	856.79	451.70	3.72	2.00	0.44
5	40338.01	271.68	14842.11	730.75	437.31	23.40	211.56	5.44
6	40446.23	468.55	14623.94	752.79	336.70	27.35	160.15	11.79
8	40562.93	491.37	14738.48	740.04	257.27	11.93	92.35	11.85
10	39607.38	649.70	14163.82	687.32	270.32	13.17	94.43	11.81
12	35018.41	1346.01	14177.40	699.72	254.81	8.46	86.77	9.63

Table A.22 Mg concentration changes in NVSs and NVS extrats (Fig. 4.36).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	2943.42	52.04	2301.91	15.43	110.65	5.39	62.48	3.30
0.5	2520.46	62.71	2353.00	13.62	80.95	5.92	58.31	2.79
1	2122.08	15.70	2198.21	18.81	70.66	4.44	60.90	3.11
2	2027.25	18.60	2461.90	9.06	48.91	1.67	56.49	2.58
3	1668.91	26.61	2266.09	15.12	56.95	2.50	54.00	2.31
4	2032.40	16.69	2035.03	22.51	56.17	2.43	38.25	0.39
5	1838.75	22.13	1893.94	25.75	49.34	1.76	36.81	0.16
6	1593.92	75.19	2235.41	19.03	28.37	0.51	35.65	0.26
8	1492.03	29.48	2046.90	24.25	21.50	0.71	28.98	0.33
10	1326.14	30.64	1728.10	29.60	22.21	0.06	26.04	0.40
12	1452.51	9.45	1583.62	74.71	22.08	0.31	28.37	0.51

Table A.23 Na concentration changes in NVSs and NVS extrates (Fig. 4.39).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	41059.73	843.23	26310.58	410.71	0.86	1.3E-01	0.17	5.7E-02
0.5	42395.24	1079.74	27339.86	383.16	1.23	8.9E-02	0.07	4.2E-02
1	42698.44	1195.70	27001.75	431.77	0.72	8.2E-02	0.61	3.6E-02
2	41172.26	1083.52	27035.86	363.12	0.61	8.1E-02	0.94	4.1E-02
3	42014.89	933.83	26941.87	465.52	0.47	5.5E-02	0.82	3.6E-02
4	40091.76	1077.40	26792.22	431.04	0.47	7.0E-02	1.14	3.8E-02
5	39970.30	1176.71	25887.74	378.85	0.30	5.1E-02	0.87	7.3E-02
6	42899.99	2115.31	25906.85	348.49	0.48	3.0E-02	0.89	2.2E-02
8	40914.12	1087.27	25681.61	471.45	0.49	4.4E-02	1.11	4.5E-02
10	40938.59	1093.43	26410.54	374.11	0.41	2.2E-02	0.52	6.1E-02
12	40521.37	1010.17	25652.17	258.47	0.46	7.8E-02	0.46	7.8E-02

Table A.24 Al concentration changes in NVSs and NVS extrates (Fig. 4.41).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	39013.56	849.91	16181.63	348.01	0.24	6.3E-03	0.05	3.6E-03
0.5	39235.51	875.94	16820.97	391.40	0.22	4.7E-03	0.07	3.6E-03
1	38104.55	810.11	16680.46	352.63	0.18	5.9E-03	0.06	3.7E-03
2	39359.66	893.65	16903.34	399.32	0.23	3.1E-03	0.07	3.2E-03
3	42022.41	1053.91	16702.39	314.95	0.22	2.4E-03	0.05	4.5E-03
4	38198.38	854.71	16695.38	352.34	0.22	3.5E-03	0.06	4.1E-03
5	36993.01	812.98	16183.08	371.30	0.15	1.5E-03	0.13	5.7E-04
6	36680.41	881.15	16181.38	378.17	0.11	2.4E-03	0.16	2.5E-03
8	38497.13	830.79	16008.75	336.95	0.10	3.5E-04	0.08	2.4E-03
10	36950.09	799.10	16609.03	395.78	0.10	7.6E-04	0.09	1.9E-03
12	37580.09	825.88	16037.23	367.95	0.10	3.5E-04	0.08	2.4E-03

Table A.25 Fe concentration changes in NVSs and NVS extrates (Fig. 4.42).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	339.72	7.08	987.59	33.25	6.2E-03	7.4E-04	3.0E-03	4.9E-04
0.5	350.18	7.03	1007.98	34.00	4.4E-03	7.6E-04	5.3E-03	3.8E-04
1	336.96	6.48	996.70	33.31	4.7E-03	5.3E-04	4.7E-03	4.0E-04
2	349.85	6.93	1014.79	34.84	3.7E-02	2.7E-03	3.7E-03	6.4E-04
3	346.16	6.93	1001.09	34.61	5.3E-02	2.6E-03	2.9E-03	5.0E-04
4	339.31	7.12	975.24	33.57	3.7E-02	2.6E-03	3.0E-03	1.2E-04
5	334.74	6.56	958.90	31.98	3.2E-02	3.1E-03	2.0E-01	3.5E-03
6	344.46	22.76	976.27	33.65	2.1E-02	2.8E-03	1.7E-01	2.5E-03
8	351.47	7.14	982.43	33.33	1.5E-02	2.0E-03	9.6E-02	1.4E-03
10	332.21	6.52	984.08	33.36	2.3E-02	1.6E-03	9.5E-02	1.0E-03
12	350.16	7.01	965.49	32.76	1.8E-02	1.7E-03	9.6E-02	5.6E-04

Table A.26 Mn concentration changes in NVSs and NVS extrates (Fig. 4.43).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	321.22	4.28	207.20	3.19	7.6E-01	5.7E-03	3.7E-01	4.4E-04
0.5	321.29	4.34	233.62	3.93	4.3E-01	6.0E-03	4.3E-01	4.1E-03
1	319.48	4.74	231.56	3.65	2.8E-01	4.8E-03	4.2E-01	1.8E-03
2	320.10	5.01	245.16	3.85	3.9E-02	4.3E-04	4.1E-01	6.1E-04
3	326.74	5.82	236.19	3.42	2.9E-02	2.2E-03	3.7E-01	2.1E-05
4	310.60	4.97	225.95	4.15	3.1E-02	5.7E-04	2.8E-01	3.6E-05
5	318.86	4.97	226.51	3.49	3.3E-02	2.9E-03	4.7E-02	9.9E-04
6	344.49	5.12	233.15	4.35	4.1E-02	1.5E-03	4.1E-02	6.7E-04
8	321.49	4.85	220.79	3.44	3.5E-02	5.4E-04	3.9E-02	2.0E-03
10	318.26	5.81	246.28	4.25	5.2E-02	3.6E-04	4.7E-02	9.2E-04
12	321.67	3.64	236.19	9.82	3.7E-02	4.4E-03	4.3E-02	2.6E-02

Table A.27 Ba concentration changes in NVSs and NVS extrates (Fig. 4.44).

month	NVS1 (mg/kg)		NVS2 (mg/kg)	
	mean	std. dev.	mean	std. dev.
0	8.66	6.4E-03	5.08	9.7E-03
0.5	8.35	2.4E-03	5.09	7.1E-03
1	7.61	4.9E-03	4.53	4.1E-03
2	7.81	9.5E-03	4.99	7.3E-03
3	8.14	2.2E-03	3.92	5.2E-03
4	7.25	4.3E-03	3.59	8.3E-03
5	7.76	7.1E-03	4.01	1.1E-02
6	8.14	4.1E-03	3.03	3.2E-03
8	7.96	5.4E-03	4.29	5.1E-03
10	6.21	9.7E-03	4.08	6.5E-03
12	8.09	4.3E-03	3.98	6.6E-03

Table A.28 Cd concentration changes in NVSs (Fig. 4.45).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	13.10	0.18	13.23	0.28	1.2E-01	2.6E-03	1.4E-01	2.5E-03
0.5	14.79	0.66	13.55	0.06	9.8E-02	1.0E-03	1.5E-01	7.9E-04
1	13.22	0.53	13.09	0.05	9.7E-02	3.9E-03	1.5E-01	1.7E-03
2	12.39	0.48	14.14	0.14	2.4E-02	1.8E-03	1.5E-01	2.7E-03
3	13.75	0.04	13.92	0.07	2.7E-02	2.5E-03	1.6E-01	3.7E-03
4	12.48	0.15	13.07	0.22	2.0E-02	2.5E-03	1.0E-01	2.9E-03
5	11.19	0.68	12.83	0.08	1.1E-02	2.0E-03	6.7E-02	1.9E-03
6	14.92	0.27	13.02	0.26	9.3E-03	4.0E-03	4.5E-02	2.1E-03
8	13.22	0.26	12.03	0.25	0.0E+00	0.0E+00	3.4E-02	1.5E-03
10	13.69	0.37	12.59	0.09	4.0E-03	1.1E-03	2.3E-02	2.3E-03
12	13.00	0.36	12.03	0.01	0.0E+00	0.0E+00	2.3E-02	1.0E-03

Table A.29 Co concentration changes in NVSs and NVS extrates (Fig. 4.46).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	198.68	7.28	57.71	2.71	1.9E-02	1.2E-03	2.8E-02	2.8E-03
0.5	209.66	6.56	67.08	3.31	1.4E-02	2.4E-03	2.7E-02	2.7E-03
1	203.87	8.17	66.67	3.11	2.3E-02	3.1E-03	2.0E-02	3.6E-03
2	207.04	6.44	69.78	3.58	3.4E-02	3.2E-03	3.4E-02	1.7E-03
3	205.47	7.49	66.15	3.69	3.1E-02	3.5E-03	2.9E-02	2.7E-03
4	197.90	7.15	65.64	3.09	3.0E-02	5.4E-03	3.6E-02	1.5E-03
5	199.57	6.46	65.27	2.76	3.0E-02	2.5E-03	1.4E-02	2.6E-03
6	201.72	7.29	68.64	3.81	2.2E-02	4.7E-03	1.4E-02	4.2E-03
8	207.94	8.05	62.87	3.35	1.8E-02	1.9E-03	1.2E-02	1.8E-03
10	201.57	4.99	71.61	3.91	1.9E-02	1.4E-03	8.6E-03	1.0E-03
12	200.42	7.24	64.55	3.03	1.4E-02	3.0E-03	1.2E-02	1.2E-03

Table A.30 Cr concentration changes in NVSs and NVS extrates (Fig. 4.47).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	154.95	2.79	139.13	8.82	6.40	5.5E-01	5.64	4.0E-01
0.5	137.24	3.84	154.71	10.87	5.56	4.3E-01	6.69	4.6E-01
1	122.21	4.95	153.07	10.42	3.86	2.6E-01	7.08	5.3E-01
2	122.78	5.85	172.68	13.39	0.27	2.8E-02	6.42	4.0E-01
3	117.71	8.26	158.16	10.49	0.20	2.9E-02	6.53	4.4E-01
4	119.23	6.83	149.93	9.53	0.22	2.5E-02	2.74	1.6E-01
5	113.01	7.11	156.06	10.72	0.16	2.0E-02	0.48	3.3E-02
6	109.26	8.62	165.20	11.74	0.09	1.2E-02	0.33	9.7E-03
8	124.17	6.43	98.06	3.13	0.06	9.3E-03	0.29	4.9E-03
10	161.42	4.74	120.73	6.19	0.10	9.6E-03	0.18	3.4E-03
12	120.75	6.92	118.72	6.08	0.12	5.2E-02	0.27	7.4E-02

Table A.31 Cu concentration changes in NVSs and NVS extrates (Fig. 4.48).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	143.68	0.38	36.08	0.02	4.84	3.9E-01	0.61	4.5E-02
0.5	131.80	1.99	37.56	0.98	3.93	2.8E-01	0.65	4.6E-02
1	121.90	1.19	36.25	2.82	3.03	1.5E-01	0.67	4.3E-02
2	120.79	3.66	38.53	0.33	0.40	2.0E-02	0.65	3.7E-02
3	113.31	5.29	36.21	1.65	0.43	2.7E-02	0.67	4.0E-02
4	115.33	2.48	31.20	1.71	0.45	3.5E-02	0.35	1.3E-02
5	120.19	0.16	35.10	2.66	0.30	1.2E-02	0.12	7.9E-03
6	106.75	5.36	35.51	1.12	0.17	2.9E-04	0.09	1.2E-02
8	119.21	3.03	31.09	1.28	0.13	6.7E-03	0.07	1.5E-02
10	118.89	1.01	34.62	3.14	0.18	6.1E-03	0.05	9.1E-03
12	116.73	2.60	30.55	1.26	0.15	2.3E-02	0.04	9.1E-03

Table A.32 Ni concentration changes in NVSs and NVS extrates (Fig. 4.49).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	111.18	4.03	104.18	1.10	1.7E-01	9.1E-03	1.1E-01	6.3E-03
0.5	121.68	1.69	108.05	6.89	1.5E-01	8.6E-03	1.4E-01	6.1E-03
1	113.15	5.14	106.68	4.12	9.0E-02	4.7E-03	1.9E-01	5.8E-03
2	116.18	6.34	111.87	6.07	0.0E+00	0.0E+00	1.6E-01	1.1E-02
3	118.50	3.10	108.97	4.00	0.0E+00	0.0E+00	1.6E-01	1.2E-02
4	108.93	4.66	108.58	4.55	1.1E-02	6.6E-03	6.1E-02	1.9E-02
5	107.94	5.06	101.34	2.19	2.0E-02	7.9E-03	9.0E-03	0.0E+00
6	99.77	1.93	109.31	4.21	0.0E+00	0.0E+00	1.8E-02	6.3E-03
8	112.58	7.36	102.18	4.34	1.5E-03	0.0E+00	1.9E-02	5.4E-03
10	107.92	4.72	110.75	3.83	0.0E+00	0.0E+00	0.0E+00	0.0E+00
12	109.65	2.63	108.60	1.10	1.5E-03	0.0E+00	0.0E+00	0.0E+00

Table A.33 Pb concentration changes in NVSs and NVS extrates (Fig. 4.50).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	523.80	15.76	176.99	5.37	0.82	4.7E-02	0.67	2.3E-02
0.5	537.49	16.10	220.75	4.40	0.70	3.8E-02	0.70	2.3E-01
1	522.46	10.85	205.00	5.88	0.61	4.6E-02	1.03	2.1E-02
2	536.46	10.62	222.90	5.50	0.51	3.1E-02	0.82	3.2E-02
3	527.18	8.65	199.85	4.75	0.61	8.2E-03	0.94	1.7E-02
4	505.15	7.32	194.02	3.44	0.47	1.8E-02	0.64	6.7E-02
5	509.68	11.18	200.12	4.70	0.60	2.9E-02	0.56	1.3E-02
6	514.91	7.46	212.92	2.96	0.56	3.9E-02	0.75	8.9E-02
8	529.59	6.21	199.13	6.83	0.53	1.5E-02	0.61	3.9E-02
10	510.10	9.51	225.33	4.39	0.49	2.9E-02	0.61	3.0E-02
12	511.58	7.41	190.79	3.39	0.30	8.3E-02	0.30	4.4E-02

Table A.34 Zn concentration changes in NVSs and NVS extrates (Fig. 4.51).

month	NVS1 (mg/kg)		NVS2 (mg/kg)	
	mean	std. dev.	mean	std. dev.
0	7.39	0.07	4.64	0.16
0.5	7.28	0.03	4.77	0.08
1	7.31	0.19	4.81	0.06
2	7.27	0.12	4.66	0.12
3	7.17	0.11	4.67	0.03
4	7.16	0.17	4.65	0.17
5	7.30	0.04	4.46	0.05
6	6.89	0.18	4.44	0.21
8	7.27	0.21	4.57	0.23
10	7.32	0.08	4.61	0.16
12	7.17	0.19	4.77	0.21

Table A.35 As concentration changes in NVSs (Fig. 4.55).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	377.90	27.03	133.21	24.31	0.97	0.82	0.05	0.05
0.5	324.34	25.79	204.66	14.97	1.58	0.80	0.04	0.05
1	325.11	25.09	147.66	23.17	1.04	0.76	0.28	0.07
2	346.78	28.21	215.18	13.24	4.08	0.27	0.85	0.04
3	299.81	32.08	176.96	22.35	4.28	0.14	0.22	0.06
4	373.37	30.42	207.46	12.40	4.08	0.23	0.93	0.03
5	340.18	29.41	118.63	22.52	3.77	0.22	2.12	0.63
6	337.44	41.39	203.99	8.26	3.44	0.14	2.53	0.39
8	285.12	17.24	233.99	9.64	3.19	0.07	2.31	0.20
10	279.24	14.50	130.95	18.11	3.13	0.01	1.81	0.27
12	280.20	16.94	120.51	22.88	3.14	0.00	1.80	0.26

Table A.36 B concentration changes in NVSs and NVS extrates (Fig. 4.56).

month	NVS1 (mg/kg)		NVS2 (mg/kg)		NVS1 Extracts (mg/L)		NVS2 Extracts (mg/L)	
	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
0	17.89	1.12	14.01	0.94	1.3E-01	3.1E-02	2.1E-01	2.7E-02
0.5	17.00	0.46	14.83	0.62	1.1E-01	3.9E-02	2.3E-01	2.7E-02
1	15.96	1.30	16.30	0.49	4.6E-02	2.0E-02	2.4E-01	1.8E-02
2	16.92	0.78	13.56	0.50	3.1E-01	1.9E-02	2.5E-01	2.4E-02
3	15.27	0.99	14.01	0.19	3.0E-01	1.1E-02	2.6E-01	2.0E-02
4	15.92	0.58	14.70	1.30	2.8E-01	1.2E-02	2.8E-01	2.1E-02
5	12.00	0.48	16.10	0.75	2.5E-01	1.8E-02	4.0E-01	2.3E-02
6	12.57	0.31	11.22	1.03	2.0E-01	7.9E-03	3.4E-01	1.8E-02
8	12.40	1.26	11.35	0.49	9.9E-02	9.7E-03	2.0E-01	1.2E-02
10	12.04	0.63	10.88	0.96	1.4E-01	1.2E-02	2.0E-01	2.6E-02
12	12.19	0.54	11.16	0.25	1.2E-01	2.6E-03	2.1E-01	2.7E-02

Table A.37 Mo concentration changes in NVSs and NVS extrates (Fig. 4.57).

month	NVS1 (mg/kg)		NVS2 (mg/kg)	
	mean	std. dev.	mean	std. dev.
0	132.95	3.51	48.35	1.07
0.5	137.38	1.39	49.35	1.39
1	134.71	4.66	49.32	6.87
2	134.92	8.85	48.96	1.56
3	133.39	3.96	48.97	0.53
4	131.37	1.52	48.96	3.64
5	129.09	1.02	47.09	2.45
6	112.73	5.71	47.16	1.95
8	124.90	3.10	47.05	2.53
10	119.53	3.54	47.95	2.93
12	112.00	6.68	47.05	1.24

Table A.38 V concentration changes in NVSs (Fig. 4.58).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	6.78	0.25	5.92	0.19	5.15	0.33
5-15	6.67	0.20	5.05	0.37	5.69	0.08
15-30	6.75	0.33	5.58	0.30	5.99	0.07
30-60	6.72	0.14	6.32	0.18	6.48	0.13

Table A.39 Soil pH under NVS piles (Fig. 4.60).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	0.06	0.01	2.20	0.08	0.90	0.11
5-15	0.04	0.00	2.26	0.10	0.43	0.03
15-30	0.03	0.01	1.53	0.08	0.28	0.02
30-60	0.03	0.01	0.45	0.08	0.17	0.02

Table A.40 Soil EC under NVS piles (Fig. 4.61).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	29208.71	1845.39	27817.48	1872.48	31345.72	2241.43
5-15	30177.07	1969.97	31642.93	2534.15	33378.00	2069.43
15-30	31521.49	3757.33	35661.47	6691.18	35651.38	1791.98
30-60	42606.29	1389.36	45926.27	1590.94	44594.15	1842.53

Table A.41 Al concentration in soils under NVS piles (Fig. 4.64).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	34.11	2.35	34.49	2.21	30.96	2.12
5-15	34.69	2.63	32.35	4.22	37.36	5.29
15-30	40.46	1.53	33.49	1.29	36.09	2.70
30-60	58.79	10.07	67.31	5.70	65.68	5.72

Table A.42 B concentration in soils under NVS piles (Fig. 4.65).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	191.82	16.43	160.17	7.13	207.62	28.83
5-15	213.90	8.42	223.79	11.31	249.51	2.86
15-30	198.28	29.54	231.34	25.42	248.55	4.08
30-60	228.92	6.30	275.12	5.41	242.20	10.46

Table A.43 Ba concentration in soils under NVS piles (Fig. 4.66).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	3475.83	129.89	4988.17	294.03	3451.24	199.48
5-15	3593.00	330.84	3788.09	202.45	3996.97	169.83
15-30	3636.72	187.84	3531.92	159.07	3897.08	195.16
30-60	3899.52	171.84	3458.18	153.13	3777.02	155.21

Table A.44 Ca concentration in soils under NVS piles (Fig. 4.67).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	7.62	0.64	8.26	0.62	9.29	1.19
5-15	9.63	0.64	9.35	1.42	8.83	0.57
15-30	8.02	1.06	9.44	0.97	9.19	0.50
30-60	7.98	0.05	9.90	0.44	9.12	0.85

Table A.45 Co concentration in soils under NVS piles (Fig. 4.68).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	17.30	0.14	25.70	1.81	25.27	1.16
5-15	16.81	1.36	18.48	0.24	18.17	0.84
15-30	18.65	2.77	17.24	0.34	19.90	0.88
30-60	29.97	2.01	33.29	1.38	31.54	2.18

Table A.46 Cu concentration in soils under NVS piles (Fig. 4.69).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	19223.69	630.28	19977.98	902.52	20618.90	1000.23
5-15	19942.85	732.65	19953.38	807.74	20968.58	1136.92
15-30	20419.13	1001.78	21793.64	2183.52	21277.19	866.06
30-60	25815.04	2405.92	24843.35	1272.35	24917.46	1235.59

Table A.47 Fe concentration in soils under NVS piles (Fig. 4.70).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	8882.77	431.45	8430.39	681.49	9962.52	792.37
5-15	8879.69	224.13	9284.99	422.03	10174.07	689.45
15-30	8833.27	1221.46	9531.54	36.16	9937.86	217.28
30-60	13144.46	1368.93	15505.44	866.41	13928.93	1064.92

Table A.48 K concentration in soils under NVS piles (Fig. 4.71).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	3760.35	337.91	4689.02	276.58	4021.57	312.72
5-15	3747.07	327.25	4571.18	221.00	4149.83	318.10
15-30	3938.73	425.46	4584.03	232.67	4309.77	270.47
30-60	5361.97	362.04	5491.65	250.03	5580.63	264.26

Table A.49 Mg concentration in soils under NVS piles (Fig. 4.72).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	893.33	84.09	895.09	67.74	1074.39	74.58
5-15	1037.80	69.63	1079.31	69.99	1032.05	71.61
15-30	844.21	54.85	838.41	136.07	902.59	61.22
30-60	542.20	100.82	483.45	44.36	442.13	85.52

Table A.50 Mn concentration in soils under NVS piles (Fig. 4.73).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	572.77	38.75	650.37	58.43	636.63	81.69
5-15	611.66	24.33	740.80	33.45	710.06	44.12
15-30	573.19	77.71	788.40	95.22	690.07	39.54
30-60	785.05	86.80	1033.98	74.68	800.64	55.56

Table A.51 Na concentration in soils under NVS piles (Fig. 4.74).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	2.20	0.34	11.77	1.43	4.28	1.39
5-15	2.72	0.31	7.19	1.19	3.62	1.51
15-30	2.65	0.26	3.66	0.71	5.27	0.85
30-60	18.32	3.47	19.40	2.96	18.47	2.38

Table A.52 Ni concentration in soils under NVS piles (Fig. 4.75).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	704.15	35.56	743.22	41.38	655.13	92.73
5-15	667.14	22.49	710.40	23.74	687.20	9.07
15-30	550.63	54.44	551.71	4.54	538.14	11.98
30-60	344.83	28.65	360.08	10.53	359.98	6.52

Table A.53 P concentration in soils under NVS piles (Fig. 4.76).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	164.05	13.27	2740.03	301.17	575.33	115.20
5-15	104.97	7.63	2562.42	110.78	494.67	43.23
15-30	76.21	15.37	1545.42	58.42	417.82	51.37
30-60	6.49	3.86	368.26	76.03	246.97	13.01

Table A.54 S concentration in soils under NVS piles (Fig. 4.77).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	36.29	1.55	32.55	2.67	38.13	5.38
5-15	39.09	1.06	40.32	3.70	44.08	0.94
15-30	41.54	6.60	48.85	13.48	48.61	2.38
30-60	59.99	1.89	67.12	0.79	67.01	1.67

Table A.55 V concentration in soils under NVS piles (Fig. 4.78).

Depth (cm)	Control		NVS1		NVS2	
	mean	std. dev.	mean	std. dev.	mean	std. dev.
0-5	11.76	2.52	16.87	1.31	15.94	2.97
5-15	10.67	0.14	11.80	0.24	15.07	0.90
15-30	10.51	3.42	11.13	1.19	12.98	1.83
30-60	26.28	3.26	27.12	2.29	25.80	0.42

Table A.56 Zn concentration in soils under NVS piles (Fig. 4.79).