SULFATE REDUCTION - DECREASES IN SUBSTRATE REACTIVITY AND THE IMPLICATION FOR LONG-TERM TREATMENT[1]

by

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Abstract Passive treatment of acid mine drainage with sulfate reduction processes appears to offer an inexpensive long term treatment solution. Many of the studies reported in the literature have generally been short term, 1-2 years in length, and have demonstrated that acidity can be neutralized and over 90% of the metals removed. Lifetime based on total carbon in the substrate has been estimated to be on the order of 20 to 30 years, but are these projections accurate? What happens if these systems fail?

Two types of municipal solid waste compost and yard waste compost were used to treat acid mine drainage in a field and laboratory setting since the early 1990's. Input pH ranged from 3- 4, and copper and nickel concentrations ranged from 40 - 100 mg/L. Initially acidity was neutralized and over 90% of both metals were removed. Rates of sulfate reduction have decreased from values typically reported in the literature to much lower values as readily available organic material is consumed and bacteria must attack the more refractive organic matter in the substrate. Municipal solid waste compost that was composted for only 45 days had higher sulfate reduction rates than the material composted for 180 days.

If the acid input exceeds the rate at which sulfate reduction processes can neutralize the input, alkalinity will be removed from the substrate. Once the inherent alkalinity of the substrate is removed, the pH of the output will drop and metals will be removed from the substrate. In columns where pH has dropped, metal concentrations have exceeded input values as the low pH solution removes metals from the substrate. Column performance was improved by "resting " the column, by stopping the input flow for a period of several weeks. After the column was restarted, the pH of the output increased from 4 to over 6. The addition of limestone to the municipal solid waste compost improved the substrate's ability to maintain pH and provided better metal removal than the municipal solid waste compost alone.

Additional Key Words: acid drainage, copper, nickel, trace metals, treatment lifetime.

Introduction

Acid mine drainage, which results from oxidation of sulfide minerals, has long been a serious environmental problem. Control of this problem by conventional treatment technology is an expensive and long-term commitment. Over the past decade there has been a growing interest in the use of passive treatment systems to control acid mine drainage. Passive systems offer control at substantially lower operating costs than conventional treatment plants, and can be installed at abandoned mines and in remote locations (Resinger et al., 2000; Canty, 2000; Eger et al., 2000). One type of passive system utilizes the ability of sulfate reducing bacteria to reduce sulfate to sulfide.

The reactions that occur can be represented as follows:

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$$SO_4^{-2} + 2CH_2O = H_2S + 2HCO_3^- \quad (1)$$

$$H_2S + M^{+2} = MS + 2H^+ \quad (2)$$

As a result of these reactions, metals can be removed from solution and alkalinity can be generated. Many systems have been installed which use compost or other organic waste to generate an anaerobic environment and provide a source of organic carbon (Hedin et al., 1991; Wildeman et al., 1994; Gusek, 1998). Complex organics present in the substrate are microbiologically degraded to simpler organics which are utilized by the sulfate reducing bacterial.

Sulfate reducing bacteria are ubiquitous and tolerate a wide range of environmental conditions (Postgate, 1984). Their optimal pH range has been reported to be from 5 to 9, but they can control their micro-environment even when the pH of the drainage was below 3 (Bolis et al., 1991; Gusek, 1998).

Numerous studies have documented the ability of sulfate reduction to treat both coal and metal mine drainage, but many of the early studies were conducted for only one to two years (Hedin et al., 1991; Filas et al., 1992; Straub and Cohen,1992; Dvorak et al., 1992; Wildeman et al., 1994). Initially, the results were impressive; pH increased from under 4 to over 7 and typical trace metal removal exceeded 90%. Although reported rate of sulfate reduction varied, a typical rate of 300 mmoles/m^3/day has been recommended as a design value (Eger, 1992; Wildeman et al., 1993). Lifetime estimates based on the total amount of carbon in these system suggested that the substrate should last for several decades (Hedin et al., 1991; Wildeman et al., 1993). Data collected from a long-term field and laboratory study indicates that the rate of sulfate reduction was a function of substrate and decreased over time. Although sulfate reduction may continue for an extended period, the rate may be too slow to provide adequate long-term treatment.

Methods

This study began as a field experiment to investigate the potential of readily available organic substrates to support sulfate reduction and to treat acid mine drainage (Eger, 1992; Eger and Wagner, 1995). Substrate was placed in three 208-liter barrels and treated acid drainage for up to four field seasons (1990-1993). Overall closure of the site required that the field portion of the experiment be terminated. Rather than lose the opportunity to examine the longevity of the treatment, the experiment was converted to a laboratory study.

Materials

Although a total of six substrate combinations were used in the field trial, only the results from the yard waste compost, the 45-day old municipal solid waste compost (MSW) , 180-day old municipal solid waste compost, and 180-day old municipal solid waste compost with limestone will be discussed in this paper. The other substrates were only tested in the field and were not converted to the laboratory column experiment. During the field portion of the study, the input was acid drainage from two 1000 metric ton stockpiles of Duluth Complex material, an igneous intrusive containing copper, nickel and iron sulfide minerals. Sulfide content in the two stockpiles varied from 0.63 to 0.8%S. The drainage quality decreased as the sulfide content increased. Input pH ranged from 4.6 to 5.5, and average metal concentrations over the course of the field study ranged from: 30 to 85 mg/L nickel, 12 to 82 mg/L copper, 1.6 to 4.3 mg/L cobalt, and 1.3 to 2.9 mg/L zinc. Sulfate concentrations ranged from 900 to 2100 mg/L.

When the column study began, drainage from the original stockpiles were used for the initial portion of the study. Although the drainage quality was similar to the field study when the columns started, pH in the drainage from the lower sulfur stockpile decreased, and metal concentrations approached those in the drainage from the higher sulfide stockpile. The pH decreased from around 5.5 to 4.6, while nickel and copper concentrations increased by about a factor of 6. Nickel increased from around 20 mg/L to 120 mg/L while copper increased from 6 to 40 mg/L. When the stockpile was reclaimed, drainage from another Duluth Complex stockpile was used as the input. Since the acid and metal concentrations were lower than in the original drainage, metal salts and sulfuric acid were added to adjust the pH and metal concentrations. Target values for the adjusted input were: pH 4.5-5.0, sulfate 1500-2000 mg/L, copper 40-50 mg/L, nickel 80-100 mg/L, cobalt and zinc 3-4 mg/L.

Experimental Design

For the field experiment, three or four sequential 208-liter barrels were fed with acid drainage collected from the two stockpiles (Eger and Wagner, 1995). The 45-day old municipal solid waste compost and yard waste were part of the original study which began in 1990. The 180-day old municipal solid waste compost was added in 1992. Initially all the substrates were saturated with stockpile drainage and allowed to stand for two weeks so the sulfate reducing bacteria could become established. Gravity flow was used to supply the system during the first two field seasons, but considerable variation in flow rates occurred. In 1992 a new perisaltic pump supply system was installed. Each field season, the barrels were drained in October to prevent freezing and splitting. Each spring the barrels were filled and a two-week conditioning period occurred prior to initiating flow to the system. The typical period of operation was May to October. Field data was collected from 1990-1993. No data was collected in 1994 since the site was to be completely reclaimed that year. During 1994 the barrels were filled in May and remained saturated until October when substrate samples were collected for the columns. A 20-cm diameter PVC pipe was used to collect about a 35 cm core from the center of each barrel. This material was transferred to a 10 cm diameter clear acrylic column. The goal was to create the same sequence in the laboratory as in the field. Each column initially contained about 60 cm of substrate. The columns were temporarily shut down several times during the course of the experiment; each time, they were maintained in a saturated condition until the experiment could begin again. Water was pumped into the bottom of the first column and water flowed via gravity to the remaining columns.

Sampling

Water quality samples were collected from the input and output of the last barrel once per week during the field season. Beginning in 1991, samples were also collected from the output of the first and second barrels of the 45-day old MSW and yard waste compost. These samples were collected about once every two weeks. Samples were analyzed for pH, specific conductance, alkalinity or acidity, major cations (calcium, magnesium, sodium, and potassium), trace metals (copper, nickel, cobalt, zinc), transition metals (iron, manganese and aluminum), and sulfate. Periodically, samples were collected from the outflow of the system for nutrients (BOD, TOC, NH_4-N, TKN, NO_3, Total P) and sulfide. Metal samples were digested using a microwave technique and analyzed on a Perkin Elmer 603 atomic absorption spectrophotometer. All samples were analyzed using standard chemical methods. A select set of samples were filtered and analyzed for metal and nutrient content. In the laboratory study, samples were collected from the last column about once every two weeks. Beginning in 1997 samples were collected from the intermediate columns about once per month. Parameters and methods were similar to the field phase, except that no nutrient samples were collected.

Results

Flow

The gravity feed system used in the field study could not be accurately adjusted, and as a result flow rates varied substantially during the initial phase of the study. Although average flow rates were close to the target rate of 30 mL/min, daily flow rates varied from 6-70 mL/min. Over 70 percent of all flows were between 20 and 35 mL/min. Control of flow rates increased substantially in 1992 when the pumping system was installed. Variation in flow decreased to within ±10%. Initially input flow rates to the 45-day old MSW and yard waste compost were on the order of 30 mL/min, but flow rates to the yard waste were increased to around 60 mL/min in 1992. Flow rates to the 180-day old MSW barrels were about ½ the flow rate for the other substrates (18 mL/min). The lower flow rate was chosen to provide adequate treatment for the more acidic drainage (Eger, 1992).

When the column experiment began, flows were initially set to provide about the same loading per unit volume as the field experiment. Water was pumped into the first column so the rate was fairly constant. Water flowed by gravity to the subsequent columns (similar to the field barrels) and the flow rate often fluctuated. Periodically flow was restricted in the columns and the columns had to be jarred to remove trapped gas bubbles.

Average flow was calculated by dividing the total volume through the columns by the time between samples. Since the flow rate through the latter columns varied, the average flow rate during the first phase of the column experiment ranged from 30-60 mL/hr for the 45-day old MSW to 12-38 mL/hr for the 180-day old compost with limestone. When the columns were restarted with the new stockpile drainage, all flow rates were decreased to 22-25 mL/hr. The flow rate to the yard waste and the 180-day old MSW with limestone was not changed and remained at about 25 mL through 1999. Flow to the 45-day old MSW compost was reduced to 11 mL/hr in 1998 and then to 5 mL/hr in 1999. Flow to the 180-day old MSW was reduced to about 5 mL/hr in 1999.

The number of treated bed volumes provides a measure of the length of time a material remains viable as a treatment media. One bed volume is a measure of the amount of drainage needed to completely fill the void space in the system, and the treated bed volume is the total volume of drainage divided by the total pore volume. The total number of bed volumes ranged from 191 for the 45-day old MSW compost to 302 for the yard

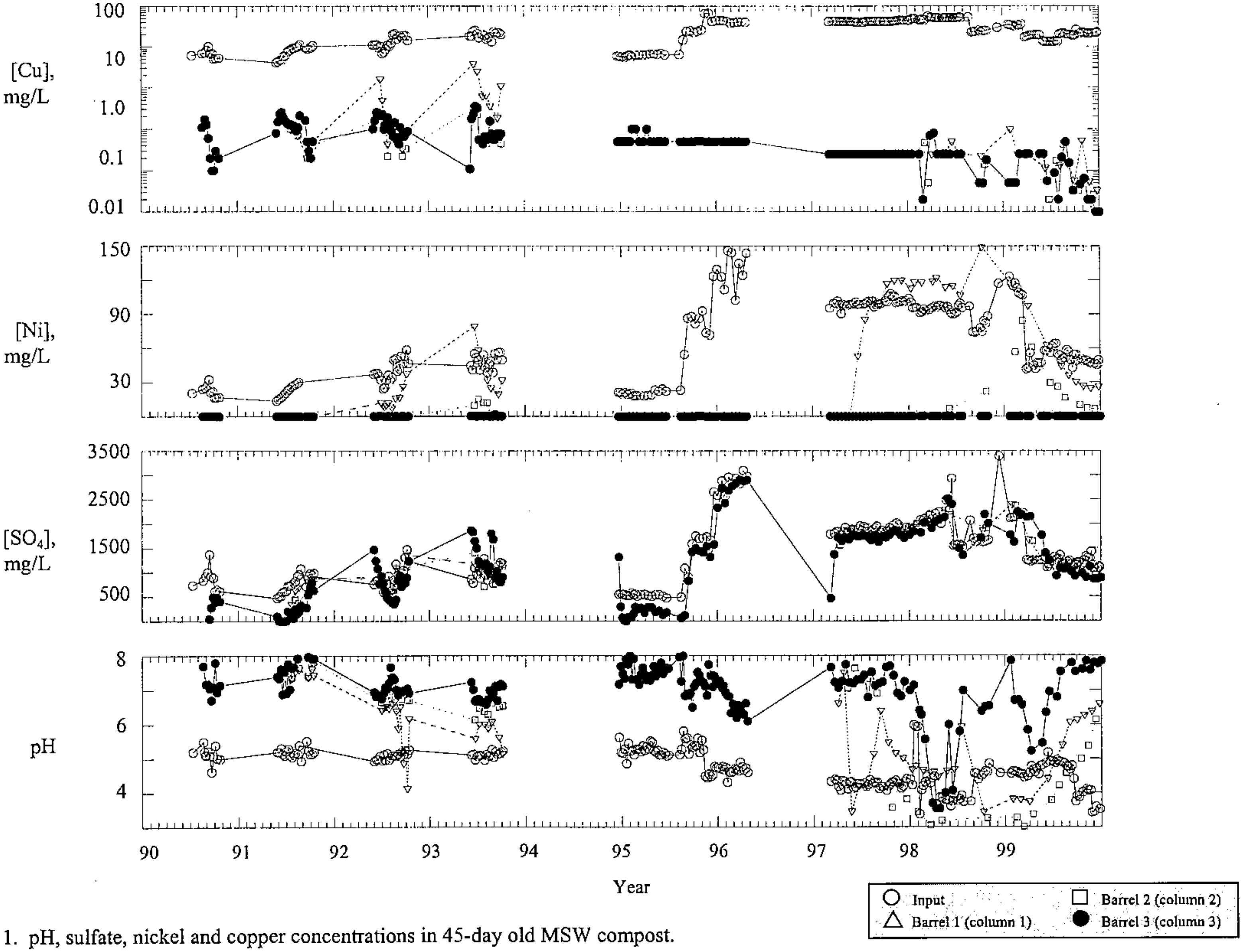

Figure 1. pH, sulfate, nickel and copper concentrations in 45-day old MSW compost.

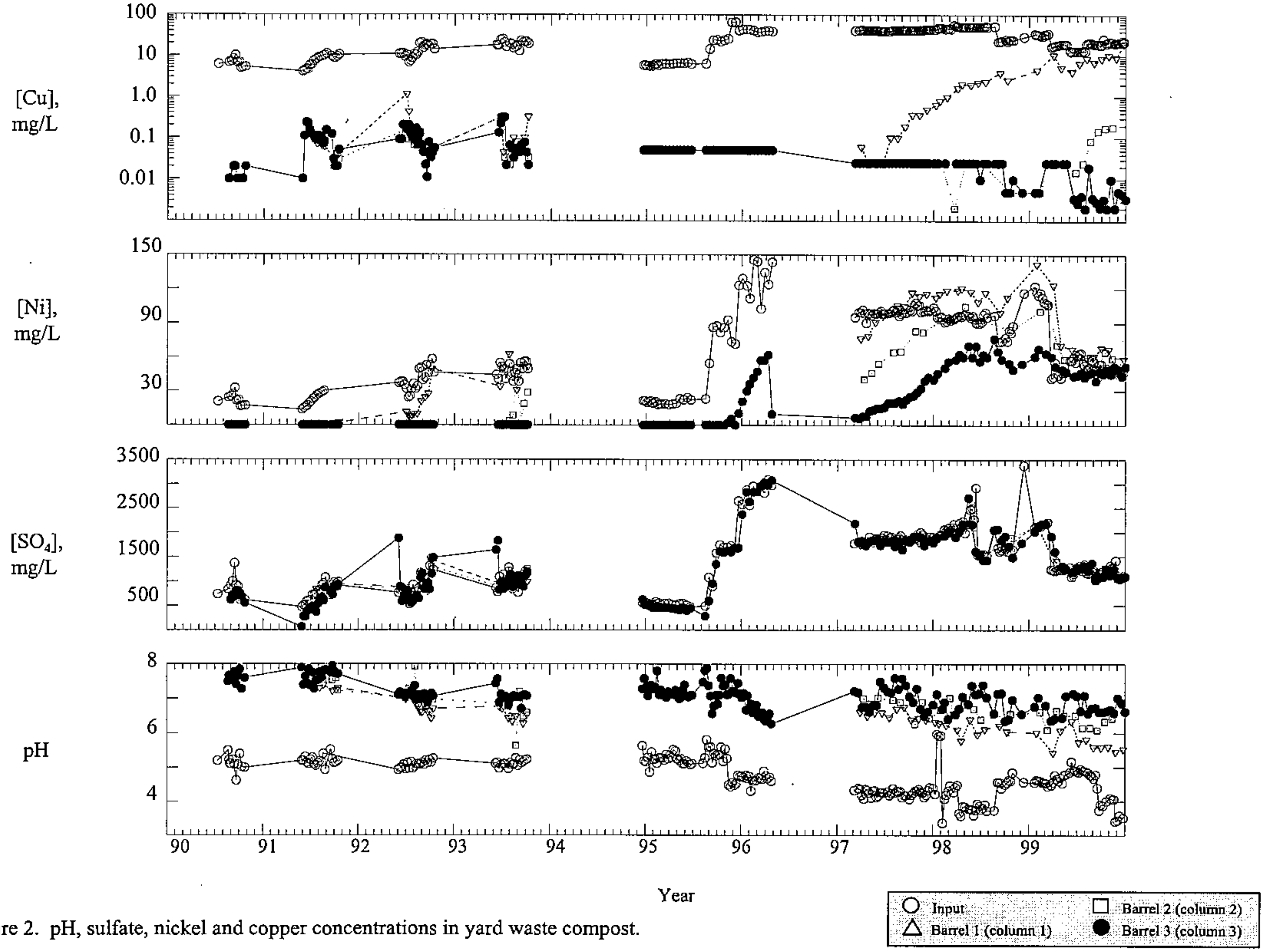

Figure 2. pH, sulfate, nickel and copper concentrations in yard waste compost.

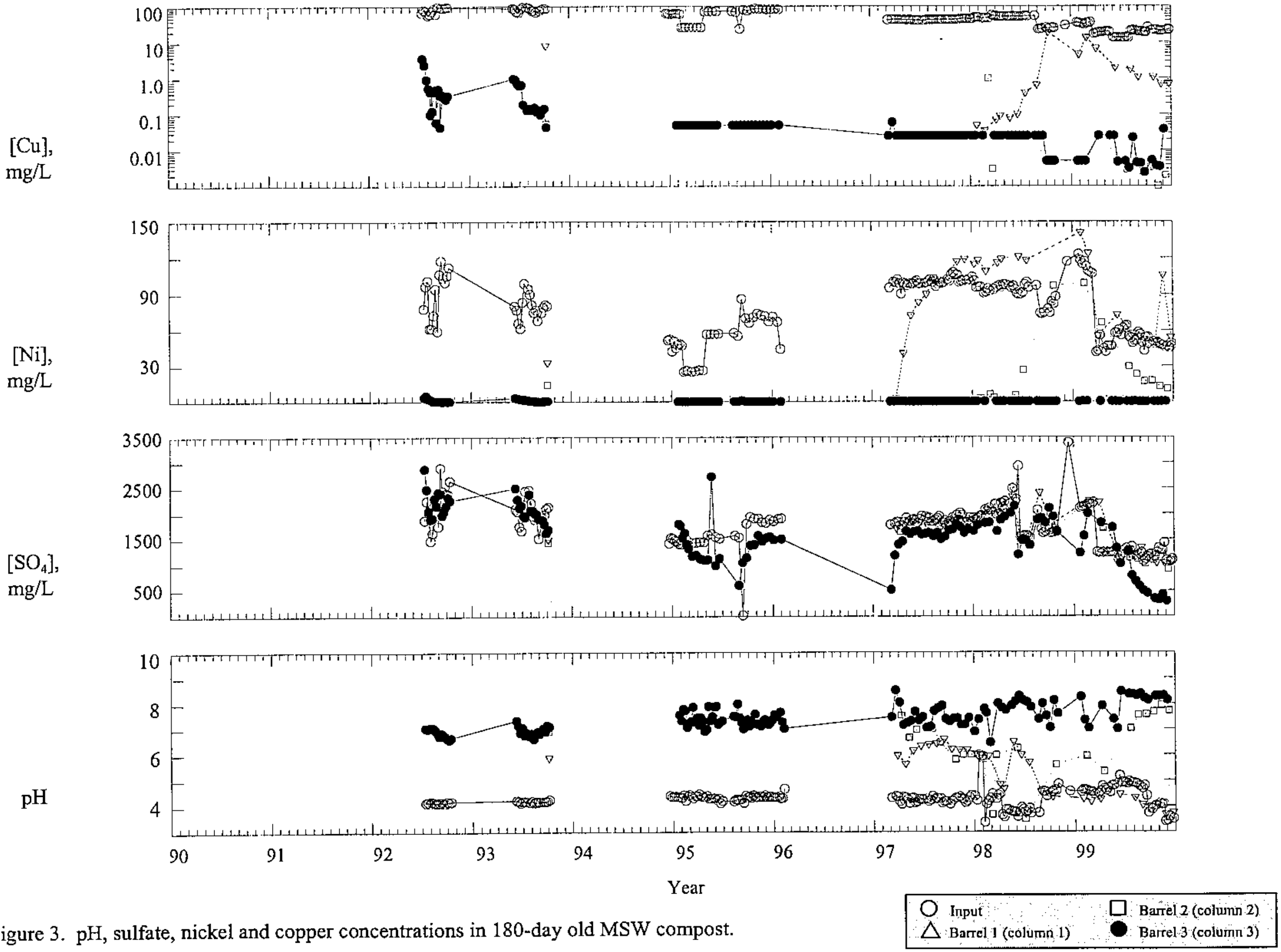

Figure 3. pH, sulfate, nickel and copper concentrations in 180-day old MSW compost.

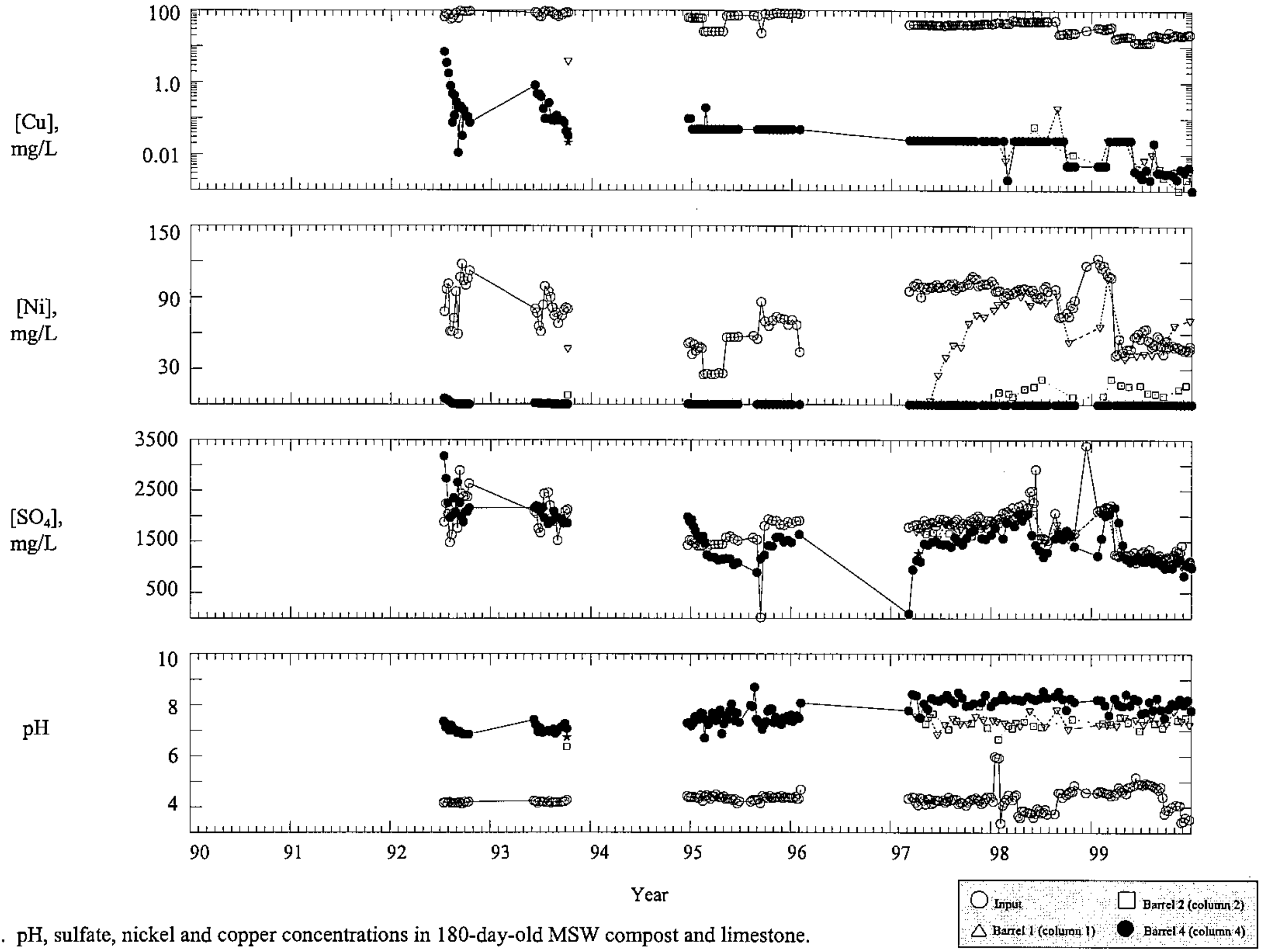

Figure 4. pH, sulfate, nickel and copper concentrations in 180-day-old MSW compost and limestone.

waste compost.

Water Quality

pH: For the field portion of the study, the pH of the drainage generally increased to over 6.5 in the outflow from all of the last barrels. Data from between the barrels in the 45-day old MSW and yard waste indicated that although pH was generally above 7.0 for the outflow from the first barrel during 1991, pH decreased each year (Figures 1, 2). By 1993, only the yard waste compost maintained pH above 6.0 as the drainage left the first barrel. The pH in the outflow of the first barrel in the municipal compost row ranged from 5.5 to 6.0.

When the laboratory columns began, samples were only collected from the outflow from the last column. For all substrates, the pH in the outflow was higher than at the end of the field study (Figures 1, 2, 3,4). The pH decreased over time in the 45-day old MSW and yard waste substrates, and was around 6 when the columns were temporarily stopped in 1996 (Figures 1, 2). The pH in the 180-day old compost columns remained fairly constant throughout this period in all columns and generally ranged from 7 to 8 (Figures 3, 4).

The pH increased in all columns after the columns were restarted in 1997. In the 45-day old MSW compost pH increased to over 7 but slowly decreased over time. Several times flow to the column was stopped and the columns were allowed to "rest." After each "rest," pH would increase temporarily but then start to decrease again. Although the pH from the last column was above 7, pH in the first two columns decreased rapidly after the columns were restarted. The pH in the first column dropped from around 7 to below 5, while the outflow from the second column produced pH in the 3 to 4 range. When the flow was reduced to 6 mL/hr in July of 1999, the pH increased and remained above 7.5 for the rest of the year (Figure 1) The pH in the other columns began to increase and was above 6.0 by the end of 1999.

For the yard waste compost, pH remained relatively constant around 7, although there appears to be a slight downward trend over time (Figure 2). The pH in the first and second columns was lower than the final column. When the columns were started in 1997 the pH in all columns was between 6.6 and 7. Although the pH in the second column was generally less than the final column, it remained above 6. The pH in the first column slowly declined over the course of the experiment and had decreased to about 5.5 at the end of 1999.

In the 180-day old MSW, the pH from the final column was generally above 7 until the flow was reduced in 1999. At that point, pH increased to around 8 (Figure 3). The pH from the first and second columns were lower than the final column. The pH in the first column dropped to values at or below the input in 1998, and have not increased despite the lower flow rate. The pH in the second column increased substantially from less than 6 to about 7.5 when the flow rate decreased (Figure 3).

The 180-day old MSW plus limestone was successful in maintaining the pH alone in all 7 columns throughout the course of the experiment (Figure 4). The pH in the first two columns was about 0.5 to 0.8 units below the output from the final column.

Sulfate: In the field study, sulfate was initially removed from the drainage by the 45-day old MSW and the yard waste compost, with the maximum removal occurring during the first year of the test. By 1992, sulfate removal had decreased and sulfate concentrations in the outflow, immediately after start up, were greater than the inflow. In 1993, there was a small net export of sulfate from the barrels. Sulfate concentrations fluctuated in the outflow from both rows with the 180-day old MSW compost. At times, sulfate in the outflow exceeded the inflow concentration.

When the columns began, sulfate concentrations in the outflow from the 45-day old MSW compost approached zero. Concentrations remained low for about 8 months until input concentrations began to increase (Figure 1). Outflow concentrations increased from around 100 mg/L to around 1500 mg/L as input concentrations increased from around 500 mg/L to around 1700 mg/L. Before the columns were temporarily shut down, input concentrations had increased to around 3000 mg/L, and output concentrations were within 5% of the input concentration.

When the columns were restarted in 1997, input sulfate was on the order of 1200 mg/L and the concentrations in the outflow from the last column were about 15% lower than the input. Outflow concentrations fluctuated in 1998 and early 1999, and sometimes exceeded input concentrations. After the columns were shut down in June of 1999 and the flow rate reduced to 6 mL/hr, the sulfate concentrations dropped to about 15 percent less than the input concentration of 1100 mg/L. Sulfate concentrations in the first and second columns followed the same general trend as the final column, but there was less difference between the input and the column concentrations (Figure 1).

The sulfate concentrations in the yard waste compost did not fluctuate like those in the MSW compost columns. Outflow concentrations in all columns were almost always within 5 percent of the inflow concentration (Figure 2).

Sulfate concentration in the 180-day old compost columns were higher then the input when the column studies began but dropped below the input after several months (Figures 3, 4). Output concentrations remained below the input when the columns were restarted with the synthetic drainage in 1997, but by 1998, there was essentially no difference between input and output concentrations. When the flow rate was decreased to the columns containing only the 180-day old MSW, sulfate decreased from the input value of around 1200 mg/L to around 300 mg/L (Figure 3).

Copper and Nickel: In the field study, all substrates successfully removed over 99% of the input metals. Output concentrations from the last barrels generally ranged from 0.05 to 0.20 mg/L for both copper and nickel (Figures 1, 2, 3, 4). Although metal concentrations in the outflows from the last barrels remained low throughout the field study, nickel and copper concentrations increased in the intermediate barrels.

For the 45-day old MSW compost, nickel concentrations increased in the outflow from barrel 1 in 1992 and in barrel 2 in 1993 (Figure 1). When the columns experiment began, overall removal was better than in the field study. Nickel concentrations in the outflow were routinely less than 0.1 mg/L, or about 50 percent lower than the field concentrations. No samples were collected from the intermediate columns until the columns were restarted in 1997. Initially there was complete nickel removal in column 1, but concentrations increased to input levels within several months. Nickel was removed from column 1 as outflow concentrations exceeded input in the latter part of 1997 and in 1998. Nickel removed from column 1 was retained in column 2 until 1998 when outflow concentrations from column 2 increased.

After the 45-day old MSW columns were shut down in June of 1999 and the flow reduced to 6 mL/hr, nickel concentration in both columns 1 and 2 decreased. About 50 percent of the input was removed in column 1, and an additional 60 percent removal occurred in column 2.

The 45-day old MSW compost has been successful in removing copper for the entire study. Although copper concentrations increased in barrel 1 in 1992 and 1993, there was no copper migration out of the system. In the beginning of 1993, copper was removed from the first barrel but retained within the second. At the end of 1993, copper moved unchanged through the first barrel. Despite this apparent saturation in the field, copper was completely removed within the first column from 1997-1999 (Figure 1). Even when pH decreased to below 5, copper concentrations did not increase.

For the yard waste compost, nickel concentrations increased in the outflow from barrel 1 in 1992 and in barrel 2 in 1993, and concentrations increased in the outflow from the last column in 1995 (Figure 2). Removal improved when the columns were temporarily shut down in 1996, since outflow concentrations were lower when the columns were restarted in 1997. Nickel was removed from column 1 in the latter part of 1997 and in 1998 when concentrations exceeded the input value. By 1998 there was no longer any nickel removal in the second column. By the end of 1999, there was no nickel removal in the entire system, as the concentration from the last column was the same as the input.

The yard waste continued to completely remove copper through 1999. Copper concentrations in the outflow from the final column were routinely less than the detection limit. Copper removal stopped in barrel 1 in 1992, but resumed in 1997 after the columns had been shut down (Figure 2). Concentrations slowly increased over time and were within 5 to 10 percent of the input concentration at the end of 1999. In 1999, copper concentrations increased slightly in column 2, but were still below 0.2 mg/L.

Although the 180-day old MSW compost columns have been successful in removing all the copper and nickel for the duration of the experiment, concentrations between the columns have varied substantially. Without the limestone, nickel increased to concentrations greater then the outflow shortly after the columns were started with the synthetic leachate (Figure 3). Concentrations decreased to the input level but no removal occurred, even after flow rates were reduced in 1999. Concentrations in the second column increased to input levels in 1998 but began to decrease when flow was reduced in 1999 (Figure 3). Copper began to increase in the first column in 1998 and had reached values equal to the outflow by the end of the year. Concentrations decreased to around 1 mg/L after the columns were "rested" and flow decreased (Figure 3).

In the MSW with limestone, the changes in concentration were delayed and although the output concentration from the first column increased to the input level, there was no nickel release from the column. Concentrations from the second column increased in 1998 but have remained at about 10 mg/L since that time. All the copper removal has occurred in the first column (Figure 4).

Sulfate Reduction Rate

The rate of sulfate reduction was calculated from the difference in input and output concentrations. Sulfate reduction rates measured for the 45-day old MSW and yard waste compost, during the first two years of the field study were generally within the range of rates measured in other investigations (Eger, 1992). However, over time rates decreased. During the last year of the field study, there was a net export of sulfate from both substrates (Eger and Wagner, 1995). The rate of sulfate reduction in the 45-day old MSW compost was two to three times that in the yard waste (Figure 5). In the field study, the outflow sulfate concentrations varied so widely in the 180-day old MSW composts that the calculated sulfate reduction rates ranged from -700 to +350 mmoles/m^3/day. The largest release of sulfate from the substrate generally occurred at the start of the season.

When the column studies began, sulfate reduction rates in the 45-day old MSW and yard waste compost were higher than the values measured at the end of the field experiment (Figures 5,6). Initially the 180-day old MSW compost columns released sulfate, but once this release ended, the rates were positive and in the same general range as the field study (Figure 5). Rates in all substrates decreased over time with the rate in the yard waste approaching zero in 1999. When the 45-day old MSW compost columns were shut down ("resting period"), sulfate reduction rates increased temporarily but generally decreased within a month. Rates ranged from around 290 mmole/m^3/day when the columns started to about 20 mmole/m^3/day at the end of 1999. The rate in the 180-day old MSW compost decreased when the synthetic drainage was added and began to fluctuate between positive and negative values, until the flow rate was decreased in 1999. After the flow rate was decreased, the sulfate reduction rate increased to around 50 mmole/m^3/day (Figures 5, 7). Although there were some negative values for the compost with limestone, values were generally positive for the duration of the laboratory phase. The value decreased from about 250 mmoles/m^3/day to about 75 mmoles/m^3/day at the end of 1999.

Discussion

Although it was possible to manipulate the MSW compost columns so that both copper and nickel were removed, the sulfate reduction rates decreased to less than 100 mmoles/m^3/day for all the MSW columns after about 275 weeks (Figure 5). By 1999, the sulfate reduction rate in the yard waste compost had decreased to 5-10% of the design rate and there was no nickel removal. Copper, which tends to form strong complexes with organic material and is less soluble than nickel at neutral pH, was still removed by the yard waste but outflow concentrations were approaching input concentrations in the first column.

Previous estimates of the longevity of sulfate reduction systems have been made based on the total amount of organic carbon in the system and have generally been reported to be on the order of at least 20 to 30 years (Hedin et al., 1991; Wildeman et al., 1993) For each mole of sulfate that is reduced, two moles of carbon are required (Equation 1). Typical values for sulfate reduction rates have ranged from 200 to 600 mmoles/m^3/day, but an average rate of 300 mmoles/m^3/day has been recommended in the design of sulfate reduction systems (Wildeman et al., 1993). Using this average sulfate reduction rate and assuming all the carbon in the substrate was available, the calculated lifetimes ranged from 21 years for the 180-day old MSW compost to 37 years for the 45-day old MSW compost.

Although the combined field and laboratory experiment spanned a total of 10 years, the number of days when the substrates actually treated drainage ranged from 5½ years for the 45-day old MSW and yard waste to 4½ years for the 180-day old compost. After 5 ½ years of treatment the sulfate reduction rate in the 45-day old MSW dropped to around 25 mmoles/m^3/day or less than 10 percent of the design rate.

Sulfate reduction is dependent on a continued supply of sulfate and small chain organic compounds produced by the decomposition of the organic matter in the substrate (Jorgenson, 1983). When the sulfate concentration exceeds 300 mg/L, the major control on the rate of reduction is the availability of organic material (Boudeau and Wostrich, 1984). Since almost all acid mine drainage contains in excess of 300 mg/L sulfate, the supply of small chain organics controls the rate of reaction. The amount of these compounds depends on the type and the reactivity ("age") of the organic substrate. Initially most organic substrates contain reactive material that can be broken down fairly quickly into small chain compounds. As the material "ages", the remaining carbon material is more difficult to break down, and the supply of small chain organics decreases. As a result, the rate of sulfate reduction decreases.

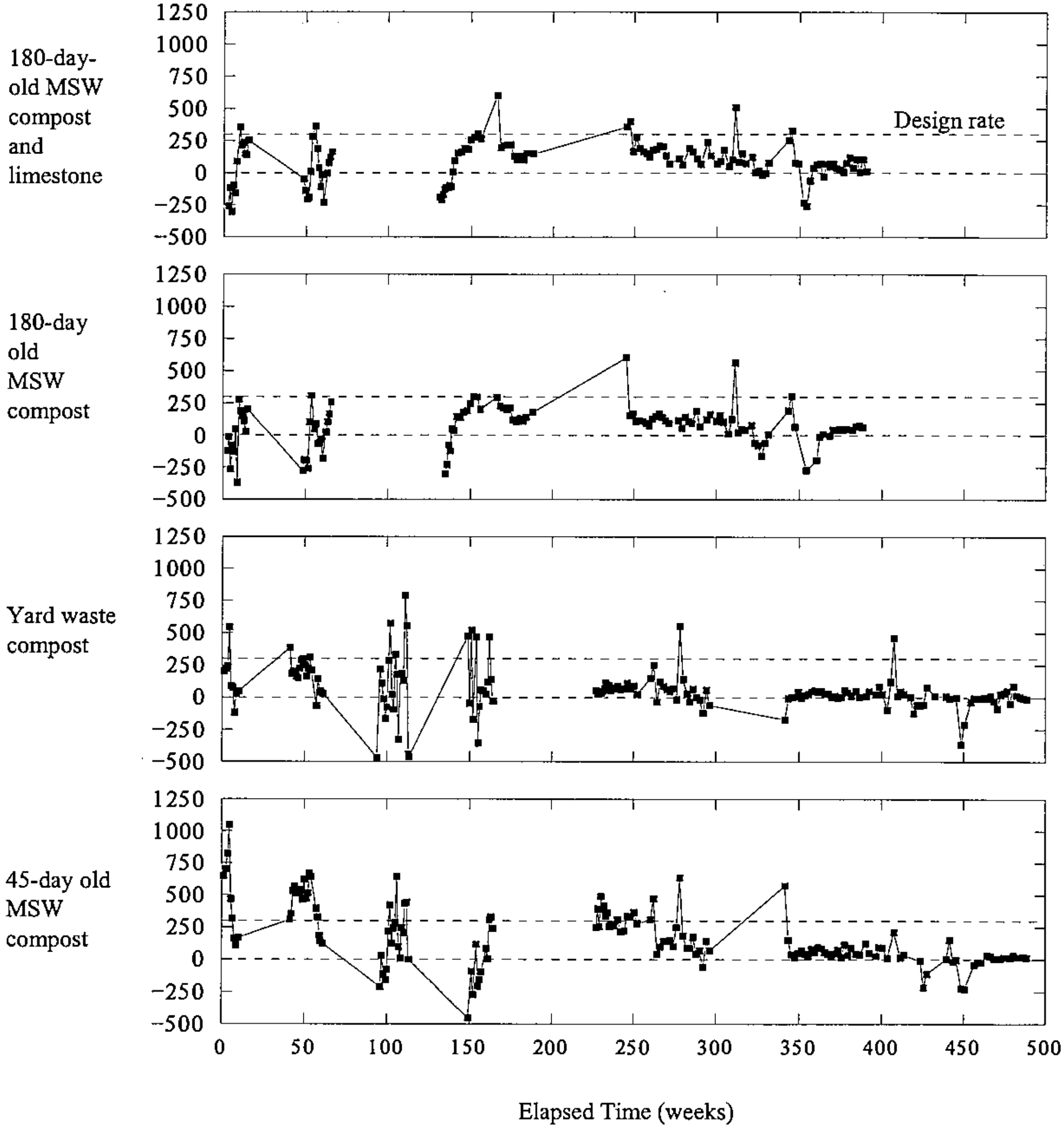

Figure 5. Sulfate reduction rates (mmol/day/m^3) in 45-day old MSW compost, yard waste compost, 180-day old MSW compost, and a combination of 180-day-old MSW compost and limestone. The y-scale has been truncated at -500 for each plot for ease of comparison; a few values (mostly early in each season) are omitted to permit better comparison of the treatments

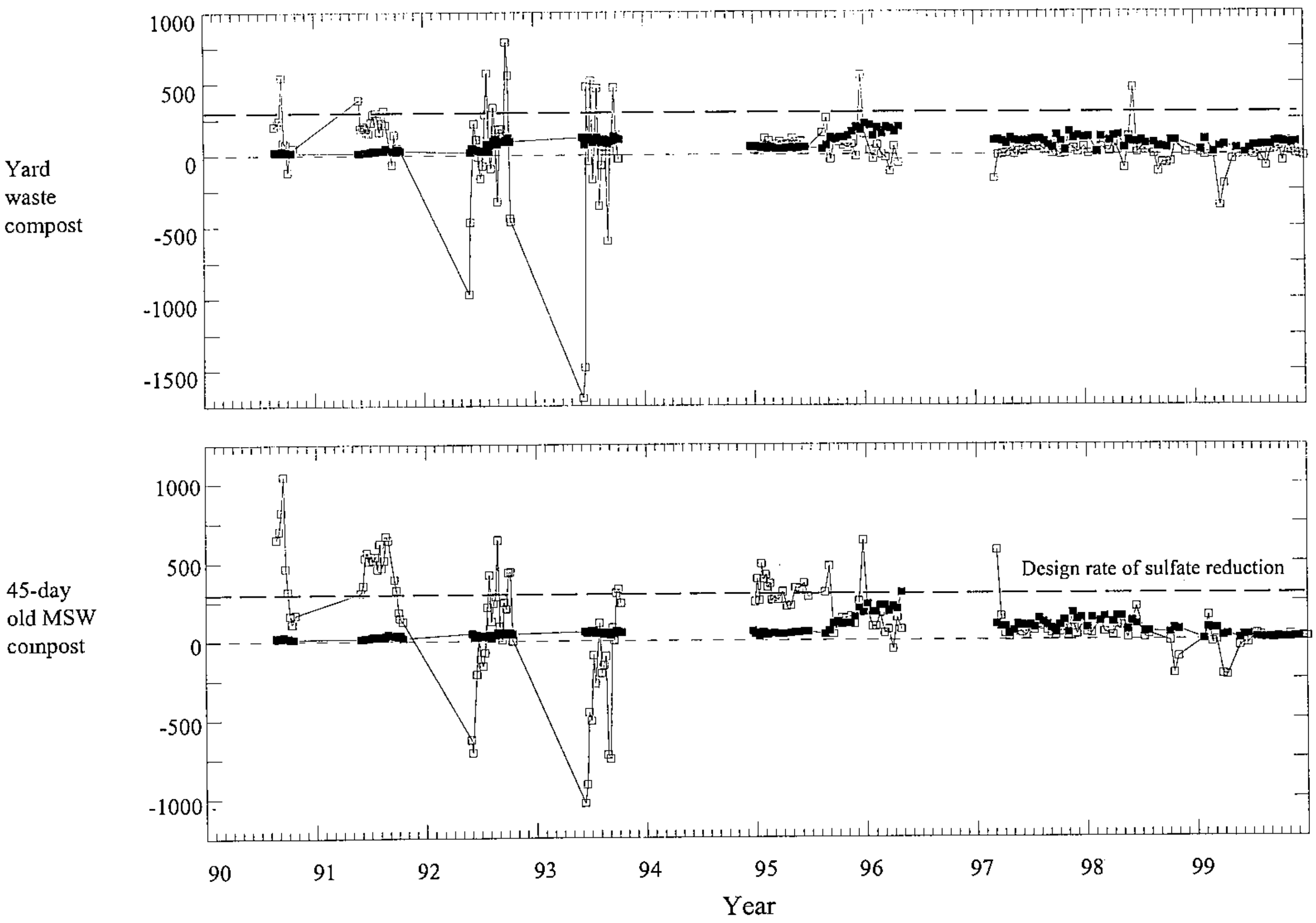

Figure 6. Sulfate reduction rate (open squares) and input acid/metal load (dark squares) in the yard waste compost and the 45-day old MSW compost; mmoles/m^3/day.

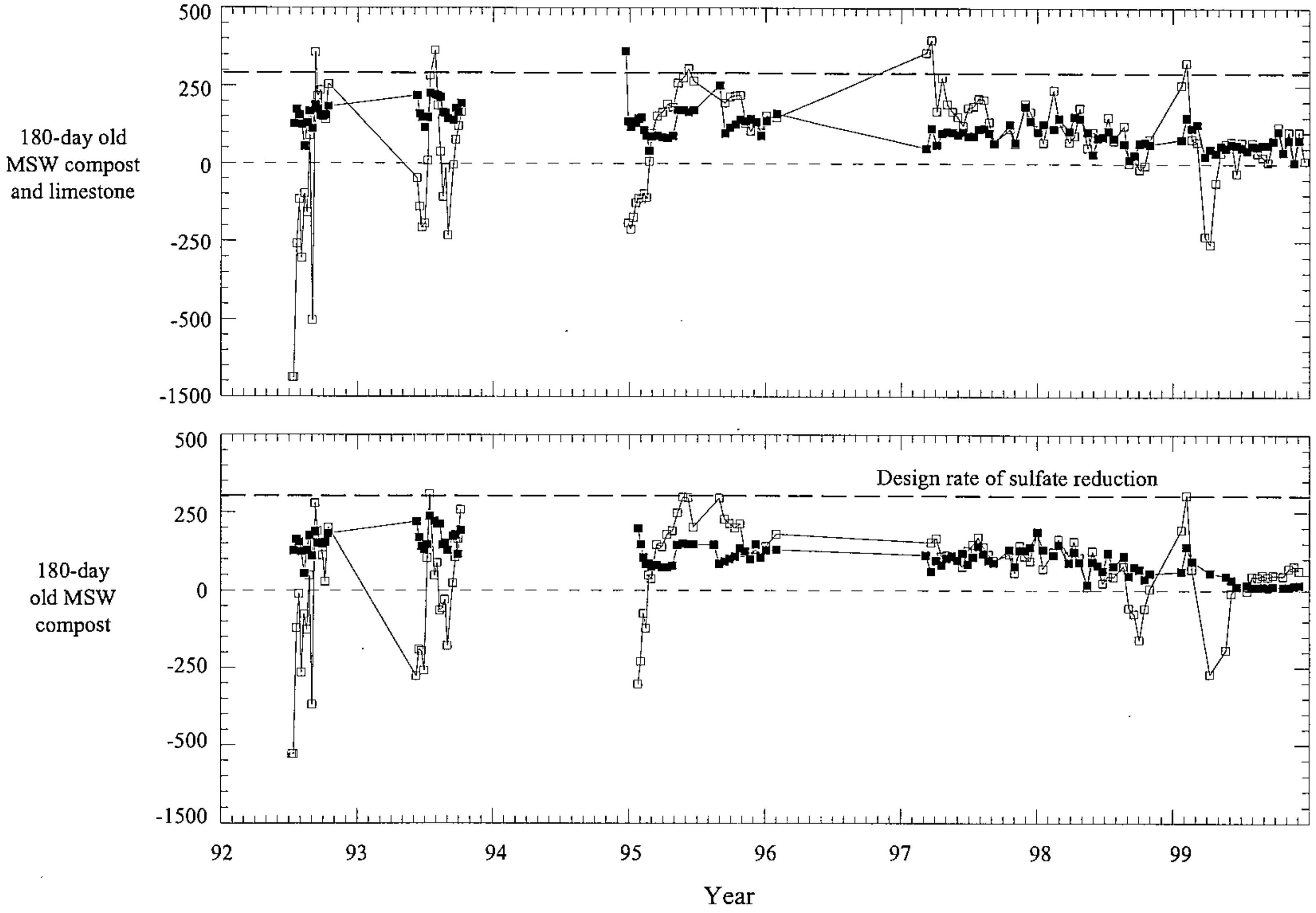

Figure 7. Sulfate reduction rate (open squares) and input acid/metal load (dark squares) in the 180-day old MSW compost and in the limestone/180-day old MSW compost mixture; mmoles/m^3/day.

Typically both municipal and yard waste compost are composted for a minimum of 180-days. This time period was chosen to insure a stable and safe material. Since the 45-day old compost had not been fully aged, it provided a more reactive substrate than the older, mature composts. Initial sulfate reduction rates were about 2 to 3 times those in the 180-day material. Even though the rates started out higher, they decreased to values comparable to the other substrates (Figure 5). The observed decrease in rate is consistent with an organic decomposition model developed by Tarutis and Unz (1994). They predicted that after three years most of the original easily decomposable organic matter would be consumed and sulfate reduction rates would decrease. In order to maintain adequate treatment, they recommended the addition of supplemental organic material every three years.

For sulfate reduction to be successful in treating acid drainage, the rate of sulfate reduction (Equation 1) must be equal to or greater than the rate of metal input. If the rate of sulfate reduction exceeds the rate of metal input, excess alkalinity is generated and the pH of the drainage increases. If the sulfate reduction system was 100 percent effective at removing metals, then one mole of sulfate would be reduced for each mole of divalent metal precipitated (Equations 1, 2). The removal of each mole of aluminum and ferric iron requires 1.5 moles of sulfate reduction (Dvorak et al., 1992; Eger, 1992). Therefore, to remove all the metals and acid in the input, the required rate of sulfate reduction can be calculated from:

$$\text{Required rate of sulfate reduction} = \text{mmole divalent metals } (M^{+2}) + 1.5\,(\text{mmole } Al^{+3}, Fe^{+3}) + 0.5\,(1000 \times 10^{-pH}) \qquad (3)$$

For the drainage in this study, copper, nickel, cobalt, and zinc were the major contaminants and accounted for about 90% of the total sulfate reduction required to treat the input water.

For the 45-day old MSW compost, the rate of sulfate reduction exceeded the input metal level in the beginning of the field and column studies, and was within the range of the typical design value of 300 mmoles/m^3/day (Figure 6). This rate exceeded the input metal load, and as a result metals were removed and pH increased. Treatment began to decline as the metal load increased (concentrations increased in the stockpile drainage) and the rate of sulfate reduction decreased.

When the metal load exceeded the rate of sulfate reduction, there was not enough alkalinity generated to neutralize the total acidity of the input. The acid neutralizing capacity of the substrate began to be depleted and outflow pH decreased and metal concentrations increased. In June of 1999, the flow rate was reduced and the rate of sulfate reduction was about equal to the rate of metal input. Metal concentrations decreased and the pH increased in all columns (Figure 1).

Although there was a large variation in the calculated sulfate reduction rates for the 180-day MSW compost, sulfate reduction rates were around 200 mmoles/m^3/day at the start of the column experiment, but by 1999 had decreased to about 50 mmoles/m^3/day. The addition of limestone to the compost supplied additional alkalinity even when the rate of sulfate reduction was less than the metal input rate. In some systems, limestone dissolution has supplied about 50% of the alkalinity, and the percentage of alkalinity contributed by limestone increased as temperature decreased (Watzlaf et al., 2000). Overall sulfate reduction rates in the columns with limestone were somewhat higher than in the columns with the compost alone (Figure 7).

The maximum sulfate reduction rate in the yard waste compost was only about one-third the value measured in the MSW compost and about one-third the typical design value of 300 mmoles/m^3/day. As a result, the metal load was almost always greater than the sulfate reduction rate (Figure 6).

Implications for Long-Term Treatment

Little long-term data is available for the performance of sulfate reduction systems but recently others have reported decreases in the rate of sulfate reduction over time (Watzlaf et al., 2000; Benner et al., 2000). Systems must be designed to compensate for a slower reduction rate as the system ages or supplemental organic matter may be needed.

The choice of substrate is also important. The reactions that occur during composting tend to consume the most readily available material. The sulfate reduction rate in the 45-day old compost was higher than the rate measured in the 180-day material. the shorter composting period provided sufficient pathogen reduction while leaving available organic material in the compost. The yard waste compost had been composted for the full 180-days, and contained about 50 percent more mineral material than the MSW compost. Based on the much slower rate of sulfate reduction, this substrate did not provide a readily available organic source to the sulfate reducing bacteria. The mineral component of the yard waste did help to neutralize the acidity of the input, as the substrate was capable of neutralizing the input for the duration of the study. Some newer systems have been constructed with materials that have been stockpiled but not composted in order to minimize the loss of the reactive organics. (Gusek, 1998)

In order to provide additional neutralizing capacity, limestone should be incorporated into the organic substrate. The limestone not only provides buffering against variation in input load, but also helps to neutralize acidity in winter when sulfate reduction rates decrease (Watzlaf et al., 2000; Benner et al., 2000). The 180-day old MSW compost with limestone treated a higher flow rate and maintained pH better than the compost alone.

Even if more reactive organic material and limestone are incorporated, it is questionable whether the substrate can maintain a sulfate reduction rate comparable to the design rate of 300 mmoles/m^3/day for an extended time. Only the 45-day old MSW could sustain sulfate reduction at a rate equal to or above the design rate, and after a total time of 250 weeks, (treatment time ~115 weeks), the rate decreased to 100 mmoles/m^3/day.

As the rate of sulfate reduction decreases either the input flow must be decreased, supplemental organic material must be added. If these changes are not made, alkalinity will be removed from the substrate. Incorporating limestone into the substrate may extend overall substrate life and provide long term removal of metals, like copper, which are relatively insoluble at neutral pH.

Conclusions

Sulfate reduction systems can provide adequate treatment for acid drainage, but the system must be designed to ensure that the total neutralizing capacity of the system (sulfate reduction plus substrate neutralizing capacity) will exceed the rate of acid input. The rate of sulfate reduction decreases over time and either the system must be designed to incorporate this decrease in rate, or provisions to replace or replenish the substrate must be made. Effective treatment lifetimes may only be about 20% of the lifetime calculated from the total carbon in the substrate.

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