Wetland Treatment Systems- How Long Will They Really Work?

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Abstract

The use of wetlands to treat mine drainage has become increasingly common; particularly as more information is available on their operation and construction. However, the lifetime of each system is still, at best, an estimate.

Treatment lifetime depends on the types of processes that provide the majority of the metal removal. Anaerobic systems (vertical flow systems) rely primarily on sulfate reducing bacteria, which reduce sulfate to sulfide and generate alkalinity. Metals can be precipitated as sulfides, and acidity is neutralized. These systems can remove over 90% of the metals and increase pH from around 4 to over 7. The bacteria will remain active as long as the system remains anaerobic and contains an adequate supply of sulfate and small chain organics. Although estimates of lifetime made on the total carbon in the system suggest that lifetime should exceed 20 years, data from field and laboratory studies show that the rate of sulfate reaction decreases with time, and that after several years rates decreased substantially. To maintain acceptable treatment, either additional organic material must be added or the total metal and acid load to the system would need to be reduced substantially.

Aerobic systems (overland flow wetlands) can effectively remove metals from neutral mine drainage by reactions with organic material in the substrate. Over 90% of the copper and nickel have been removed in aerobic systems treating mine drainage in Minnesota. The primary removal processes in these systems include adsorption, ion exchange and complexation, which are finite; removal will cease unless new removal sites are generated. At one wetland in northeastern Minnesota, the annual production of new removal sites has been estimated to be equal to the annual metal input, and, as a result, metal removal should theoretically continue indefinitely.

Introduction

Acid mine drainage, which results from the 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 use natural processes to remove metals and acidity , have lower cost and maintenance 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). The "perfect" passive system would require no maintenance and operate indefinitely.

The ability of wetlands to remove contaminants from water has long been recognized. Wetlands have often been referred to as "nature's kidney" and can successfully remove suspended material, nutrients and metals (Hammer, 1989). Geologists searching for ore deposits were among the first to observe that wetlands can accumulate metals. Concentrations of trace metals in wetlands can exceed 1000 mg/kg, and indicate the presence of a metal deposit in the watershed. Copper concentrations in some Canadian wetlands reached 2-6% (Sobolewski, 1997). Natural wetlands receiving mine drainage were also capable of removing significant amounts of metals, and appeared to offer an alternative treatment approach (Eger et al, 1980, Weider and Lang, 1982, Eger and Lapakko, 1988). Based on these observations, wetlands began to be constructed in the mid 1980's to treat various types of mine drainage.

Although many of the initial systems were designed on empirical relationships, recent designs are based on a more thorough understanding of chemical processes, and on both the successes and failures of the past. Since mine drainage problems can persist for hundreds of years, the lifetime of wetland systems is a critical issue. This paper summarizes the results from several of our recent studies which address the question of treatment longevity.

Anaerobic Systems

Anaerobic systems, also called subsurface or vertical flow wetlands, have been successfully used to treat acid mine drainage (Figure 1). These systems utilize the ability of sulfate reducing bacteria to reduce sulfate to sulfide, which leads to the removal of metals and acidity. The reactions that occur can be represented as follows:

$$SO_4 + 2CH_2O = H_2S + 2HCO_3 \quad (1)$$

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

where CH_2O represents a small chain organic compound.

Many systems have been constructed using 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 bacteria. Although wetland plants are sometimes present, many systems have been built without them.

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 bulk solution pH is below 5. Sulfate reduction treatment has been successful 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 less than 4 to over 7, and typical trace metal removal exceeded 90%. 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 indicate that these predictions may substantially overestimate the lifetime of the substrate.

A combination field and laboratory study was conducted to evaluate the ability of readily available organic substrates to neutralize acidity and remove metals from mine drainage from stockpiles of Duluth complex material. The Duluth Complex is an igneous intrusive in northeastern Minnesota which contains copper, nickel and iron sulfide minerals. The drainage quality varied with time; pH ranged from around 4.0 to 5.0, copper concentrations from 10-50 mg/L and nickel concentrations from 20-100 mg/L. Sulfate concentrations were on the order of 900 mg/L.

The study initially began as a field study using a series of three sequential 208 liter plastic barrels, but was converted to a column study when the field site was reclaimed. The laboratory study was designed to replicate the situation in the original field study and was conducted in three sequential 10 cm diameter clear acrylic columns. The material was transferred from the field to the laboratory to create the same sequence and conditions. Details on the studies are presented in (Eger and Wagner, 2001a).

Results

Although several substrates were used in the study, only the results from a 45-day old municipal solid waste compost are presented. This material was studied over a ten year period and was one of the more reactive substrates. Results for other substrates are presented in Eger and Wagner, 1995 and 2001b.

Water Quality

Initially treatment was very successful. The pH in the outflow from the overall system increased from about 5.0 to over 6.0, sulfate decreased by at least 50%, and over 99% of the input copper and nickel were removed (Figure 2). Although the system effectively removed copper and nickel for the entire experiment, sulfate removal decreased and outflow pH fluctuated, reaching a minimum of around 4 during the column study. By reducing the flow rate and periodically stopping the columns for a period of 1-2 months, treatment was reestablished and outflow pH increased (Figure 2). At the end of the experiment, the outflow pH was above 7.5 but the inflow flow rate had been reduced to about 10% of the original flow.

Sulfate Reduction Rate

The rate of sulfate reduction was calculated from the difference in input and output concentrations. Sulfate reduction rates measured during the first two years of the study were generally within the range of rates measured in other investigations (Eger, 1992). However, rates decreased over time. During the last year of the field study, there was a net export of sulfate (Eger and Wagner, 1995). When the column studies began, sulfate reduction rates were higher than the values measured at the end of the field experiment, but rates decreased over time (Figure 3). When the MSW compost columns were shut down ("resting period"), sulfate reduction rates increased temporarily but then generally decreased within a month. Rates in the MSW compost ranged from around 290 mmole/m^3/day when the columns started to about 20 mmole/m^3/day at the end of 1999.

Lifetime

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 20-30 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 average values for sulfate reduction rates range from 200 to 600 mmole/m^3/day, but an average rate of 300 mmole/m^3/day has been recommended for the design of sulfate reduction systems (Wildeman et al., 1993). Using this average sulfate reduction rate, and assuming all carbon in the substrate was available, the calculated lifetime for the MSW compost was 37 years.

Although the combined field and laboratory experiment spanned a total of 10 years, the number of days when the substrate actually treated drainage totaled about 5.5 years. Although sulfate reduction still occurred in the MSW compost, the final rate was less than 10% of the recommended design rate of 300 mmole/m^3/day.

Sulfate reduction is dependent on a continued supply of sulfate and small organic compounds produced by the decomposition of the organic matter in the substrate (Jorgenson, 1983). When the sulfate concentration exceeds 300mg/L, the major control on the rate of reduction is the availability of organic material (Bourdeau 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 also decreases. The observed rate decrease is consistent with an organic decomposition model developed by Tarutis and Unz (1994; Figure 4). 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.

Although data on the long term behavior of sulfate reduction systems are limited, there have been other reported decreases in the rate of sulfate reduction over time (Watzlaf et al., 2000; Benner et al., 2000). In several systems a supplemental carbon source was introduced to increase the rate of sulfate reduction (Miller, 2001, Anderson, 2001). Decaying wetland plants could provide some carbon to the wetland, but many systems have not encouraged plant growth. In one study, plant roots penetrated the entire bed and oxygenated the substrate, inhibiting the sulfate reducing bacteria (Gusek, 2000).

Carbon production in natural wetlands has been reported to be about 1 $kg/m^2/yr$ (Whittaker and Likens, 1972). For a 1 meter thick substrate, this would provide 23 mmole $carbon/m^3/day$. Since two moles of carbon are required to reduce each mole of sulfate, the reaction rate based on the annual input of carbon would be only about 12 $mmole/m^3/day$ or a factor of 25 less than the typical design rate of 300 $mmole/m^3/day$.

Sulfate reduction systems can provide acceptable treatment for acid drainage, but the design must account for the decrease in reaction rate with time. Unless the system is large or there is an supplemental input of available organic carbon, the substrate will have to be replaced in order to maintain the reaction rates.

Aerobic Systems

Aerobic systems, also called surface flow wetlands, were the initial type of systems constructed to treat mine drainage (Figure 5). Although they were effective in removing iron from coal mine drainage, they were not successful in increasing the pH of the drainage. As a result, the use of aerobic systems is limited to the treatment of net alkaline drainage, where pH > 6.5 and the total alkalinity > total acidity. For coal mine drainage, these systems are typically used after the alkalinity of the drainage has been increased in either an alkaline limestone trench (ALD) or in successive alkalinity producing systems (SAPS), and are primarily designed to precipitate iron as a hydroxide ($FeOH_3$). As the iron precipitates build up, the wetland fills with these solids and the treatment efficiency decreases. The overall lifetime of these systems is limited by the total volume available to collect and store the iron precipitates. The feasibility of removing these solids, recovering the iron hydroxide, and using it for paint pigments is being studied (Hedin, 1998, 2001).

Aerobic systems can also be applied to the treatment of neutral metal mine drainage. Since the solubility of most metals decrease as the pH increases, metal concentrations in neutral mine drainage are generally at least one order of magnitude lower than in acid drainage. Metal removal in aerobic systems occurs by reactions with the substrate, which include adsorption, ion-exchange and complexation. The ability of these reactions to remove metals is limited by the number of reaction sites, which is a function of the volume of substrate that the flow can contact. Unless new removal sites are generated, removal will stop when all the sites have been used.

The long term effectiveness of aerobic systems to treat neutral mine drainage has been studied at the Dunka Mine in northeastern Minnesota. A 0.7 ha system was built in 1992 to treat neutral drainage from a waste rock stockpile. The pH of the input drainage ranged from 6.7 to 7.6 with the majority of measurements between 7.0 and 7.4. When the system was first constructed, the input nickel concentration was about 5 mg/L but decreased to less than 1 mg/L after the top of the stockpile was covered with a polypropylene liner in 1995 (Eger et al., 2002). There was little change in pH as water moved through the wetland but nickel concentrations decreased. Concentrations decreased by about 90% before the stockpile was capped to around 60% after input concentrations decreased (Figure 6).

Mass removal was calculated by combining the concentration and flow data and ranged from an average of 170 kg/yr of nickel before capping to generally less than 10 kg/yr after capping. A total of about 540 kg of nickel was removed in the wetland over the eight years of the study.

Lifetime

When metals are removed by surface reactions with the substrate, the total removal will be controlled by the total number of available removal sites. Based on previous studies of peat at the Dunka Mine, the maximum removal capacity was estimated to be 10,000 mg nickel/ kg dry peat. By combining this removal capacity with the total mass of peat in the active zone of flow (Romanov, 1968), a total removal capacity of 1400 kg nickel was calculated (Eger and Wagner, 2002). The lifetime of the wetland was then estimated by dividing the total capacity by the average annual input of nickel.

Prior to capping, the average nickel load from the stockpile was 170 kg/yr and the estimated lifetime was:

Lifetime = (1400 kg) / (170 kg/year) = 8 years

When the top of the stockpile was capped, both flow and nickel concentration decreased, resulting in about a 90% decrease in the overall nickel load and an increase in lifetime from about 8 years to over 100 years.

New removal sites are generated as vegetation dies and new organic substrate accumulates. The average rate of peat accumulation in northern wetlands is about 1 mm/year (Craft and Richardson, 1993). If the removal capacity of the newly accumulated material is assumed to be 10,000 mg nickel/kg, the wetland would add 7 kg of nickel removal capacity each year. Using the average of the input load after the stockpile was capped (10 kg) as representative of the post-closure period, and assuming an annual increase of 7 kg nickel removal capacity, the projected lifetime for the wetland is about 290 years (Table 1).

If the treatment is to be sustainable and effective, not only must there be new metal removal capacity generated, but the metal must be retained within the wetland. Mass balances calculated on wetland test cells demonstrated that over 99% of the removed metals were associated with the substrate and that less than 1% of the total removal occurred in the vegetation (Eger et al., 1994). These results were consistent with earlier studies on metal removal in a white cedar wetland (Eger and Lapakko, 1988) and with data reported by others (Skousen et al., 1992, Wildeman et al., 1993). Sequential extraction tests, conducted on the test cell substrate samples, demonstrated that only 1-2% of the nickel was water soluble and therefore easily removed from the substrate (Eger et al., 1994).

Additional evidence for the permanent nature of the removal in the wetland is that nickel removal continued despite a decrease in the input concentration of almost an order of magnitude. If the nickel was weakly bound to the substrate, nickel would be released from the substrate as nickel concentrations in the water decreased, and no removal would occur. Over the seven years of operation, output concentrations have rarely exceeded input values, and there has always been a net removal of nickel in the wetland (Figure 5).

Table 1. Estimated lifetime of wetland .

Year	Annual nickel load (kg)	Percent of pre-capping load	Lifetime of wetland (years)[1]
Initial design lifetime	144	---	10
1992-1994	170	---	8
1995	76	45	18
1996	36	21	39
1997	8	5	175
1998	5	3	280 (self-sustaining)[2]
1999	16	9	88

[1] Lifetime is calculated by dividing the initial removal capacity of the wetland (1400 kg) by the annual load.
[2] Annual nickel load to the wetland is less than the estimated annual gain in nickel removal capacity (7 kg); therefore the wetland would, in theory, be self-sustaining.

Conclusions

The lifetime of wetland systems is a function of the input water quality and the type of removal processes. For anaerobic systems, removal will occur as long as a carbon source and sulfate are present in an anaerobic environment. Since problematic mine drainage generally has elevated sulfate concentrations, the limiting reactant is the amount of available carbon. For organic substrate systems, the estimated lifetime based on total carbon generally exceeds 25 years, but effective treatment is likely to last less than 5 years unless the substrate is replaced or supplemental carbon is added to the system. Internal generation of carbon from vegetation is limited and would require much larger systems than are typically built.

Removal in aerobic systems is governed by the volume available to collect and store chemical precipitates (coal mine drainage) or the number of available removal sites (neutral metal mine drainage). Although precipitated solids can be periodically removed from wetlands, only systems that are well vegetated can generate sufficient new removal sites to offer the possibility of long term, low maintenance treatment. Since the generation of new removal sites is a slow process, long term treatment will require a large wetland, with a relatively small input load.

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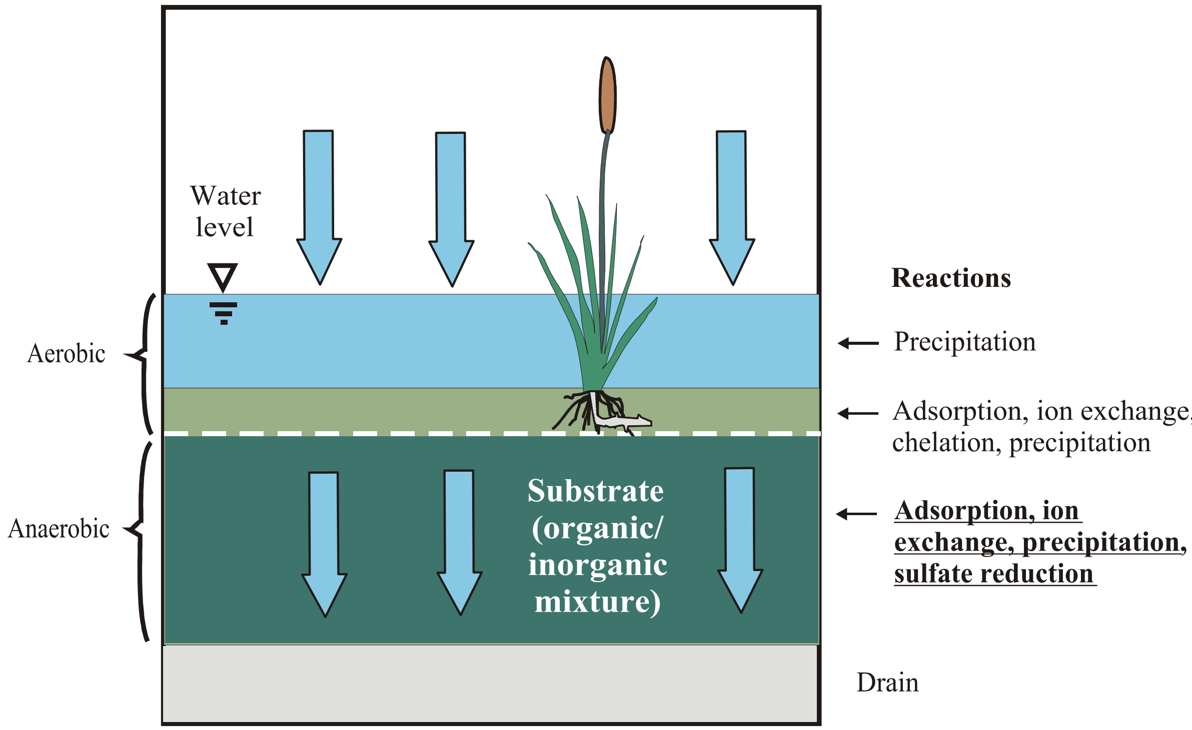

Figure 1. Anaerobic wetland; bold indicates primary removal mechanisms.

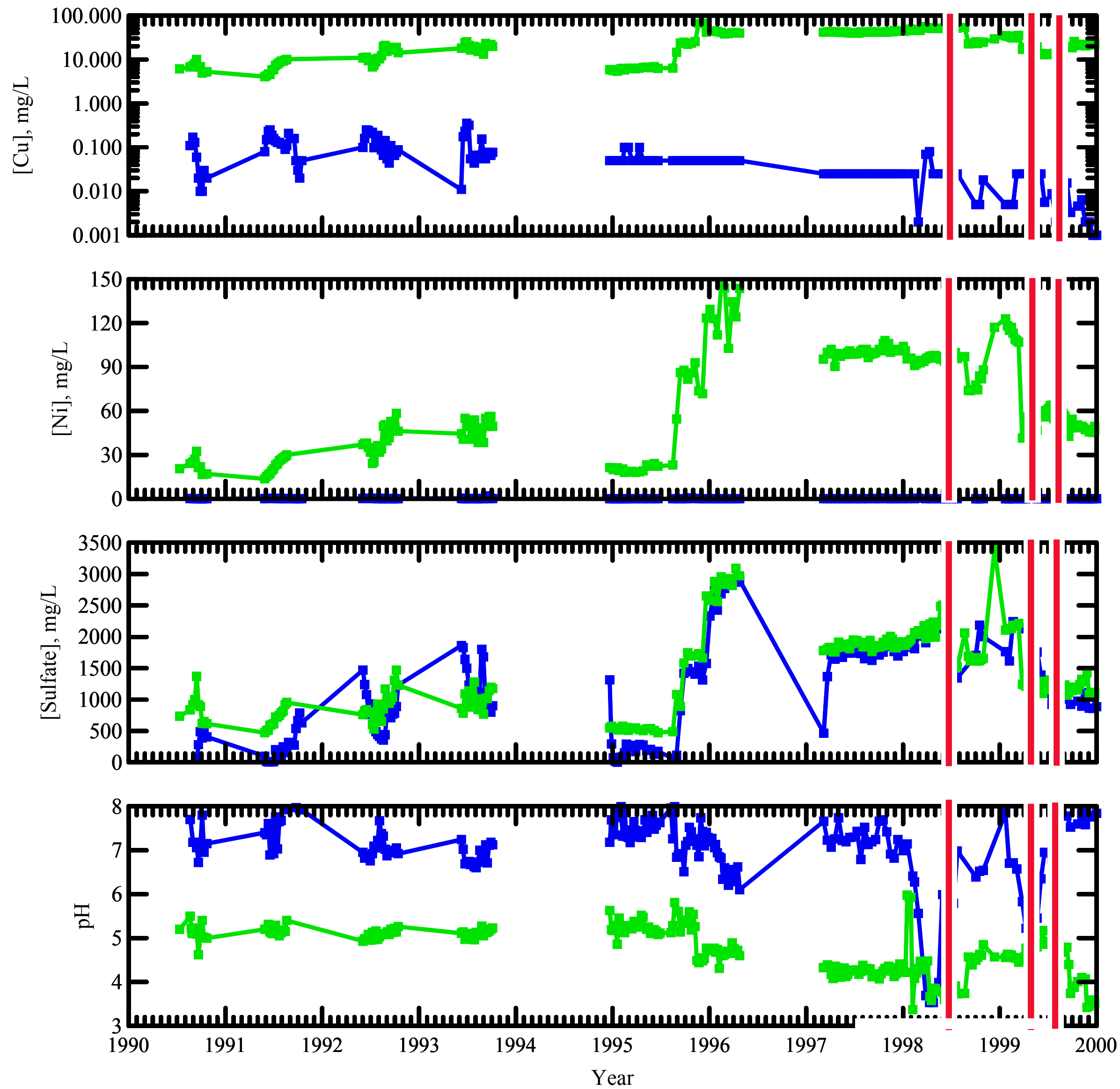

Figure 2. pH, sulfate, copper and nickel concentrations vs. time for the influent (green) and effluent (blue) of the MSW compost, 1990-2000. The vertical red lines show when the columns were rested and flow rate reduced.

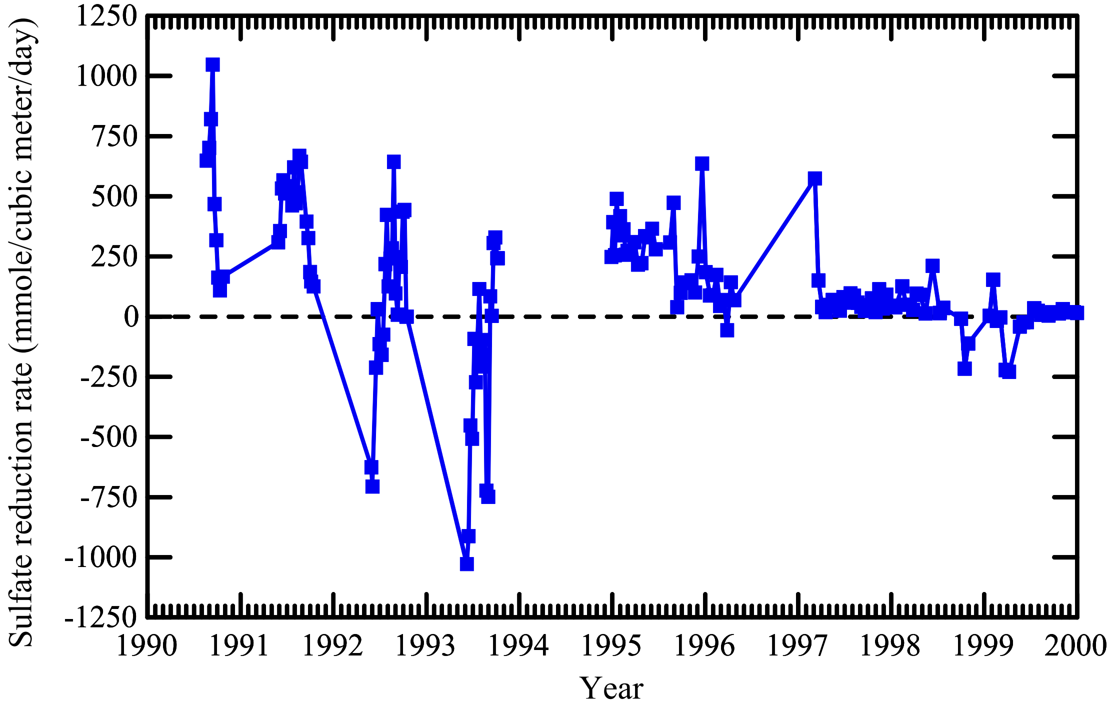

Figure 3. Sulfate reduction rate (mmoles/m^3/day) for the MSW compost.

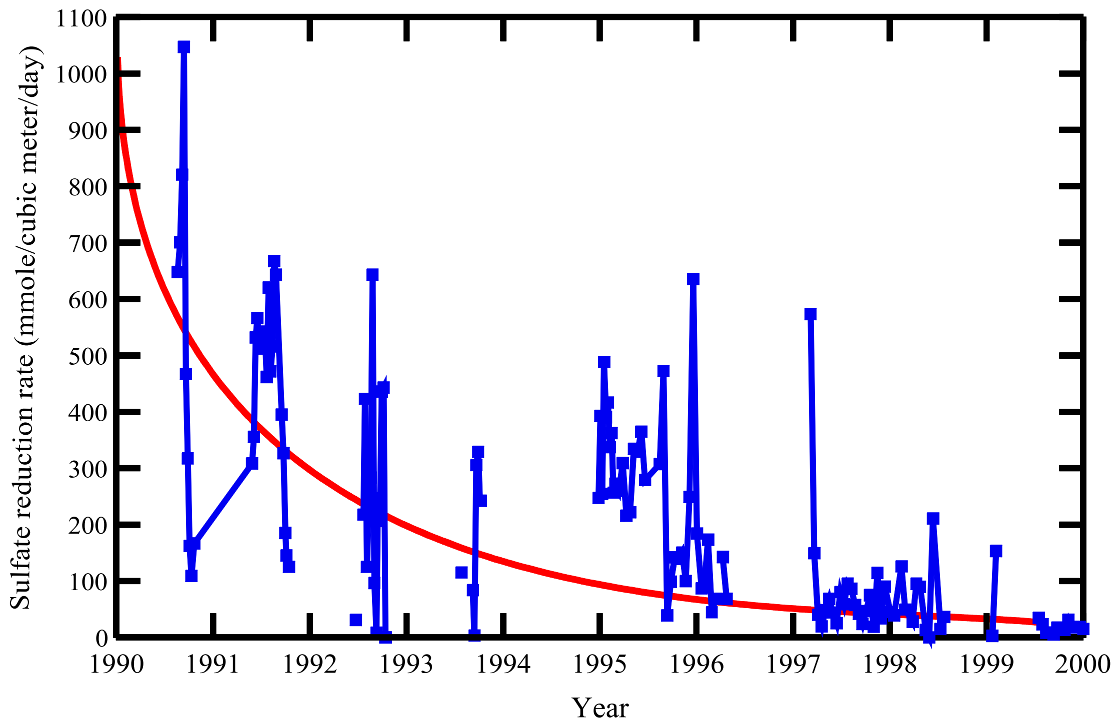

Figure 4. Sulfate reduction rate vs. time for the MSW compost. The red dashed line depicts the organic decomposition curve as calculated from Tarutis and Unz (1994). (Negative sulfate reduction values have been omitted from this graph.)

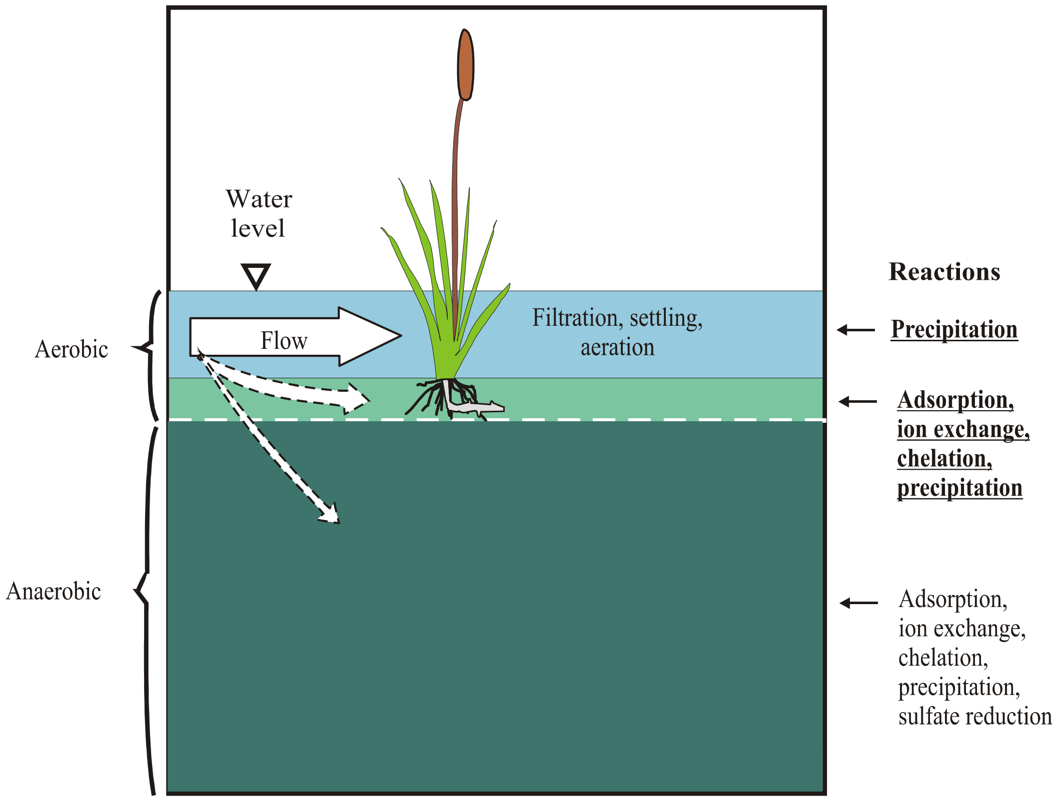

Figure 5. Aerobic wetland; bold indicates primary removal mechanisms.

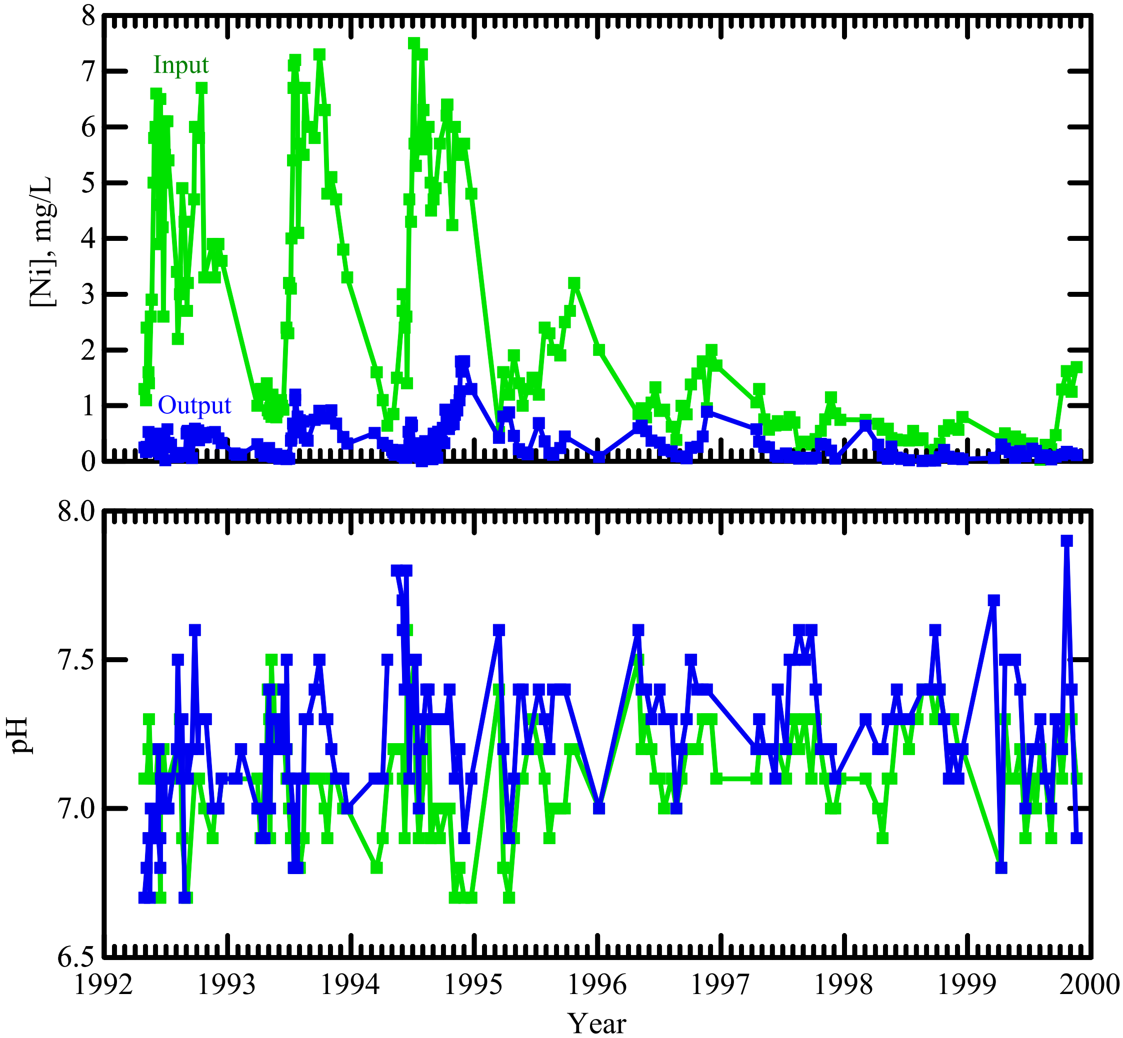

Figure 6. pH and nickel vs. time in the input (green) and output (blue) of the W1D system.