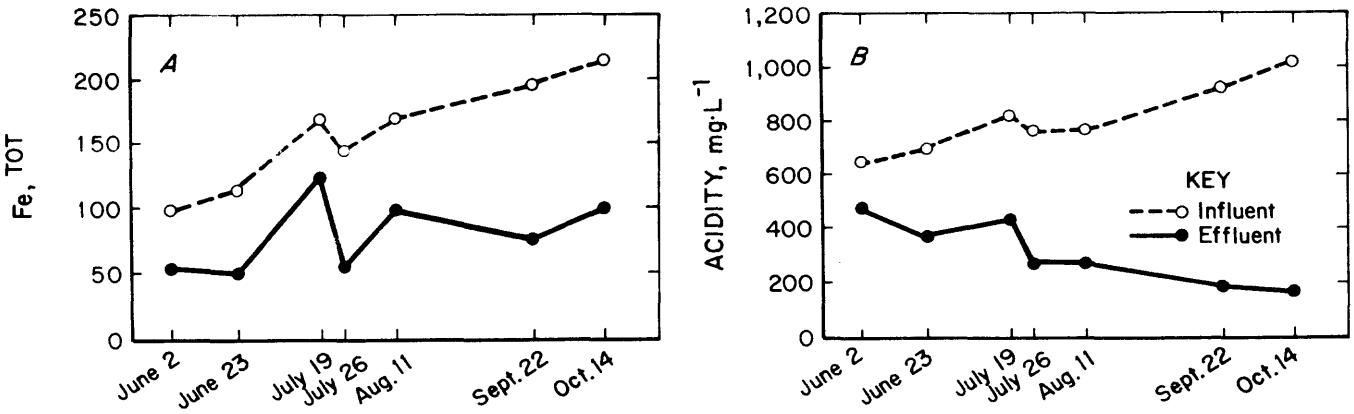

Figure 8.—Influent and effluent concentrations at the Latrobe wetland during the summer of 1988. *A*, Fe; *B*, acidity.

concentrations of dissolved Al. Instead, concentrations of Al in mine waters are primarily influenced by the solubility of $Al(OH)_3$ (*23, 43*). At pH levels between 5 and 8, $Al(OH)_3$ is highly insoluble and concentrations of dissolved Al are usually <1 mg•L^{-1}. At pH values <4, $Al(OH)_3$ is highly soluble and concentrations >2 mg•L^{-1} are possible.

The passage of mine water through highly oxidized or highly reduced environments has no effect on concentrations of Al unless the pH also changes. In those cases where the pH of mine water decreases (due to iron oxidation and hydrolysis), concentrations of Al can increase because of the dissolution of alumino-silicate clays by the acidic water. When acidic mine water passes through anaerobic environments, the increased pH that can result from carbonate dissolution or microbial activity causes the precipitation of $Al(OH)_3$.

CHAPTER 3. REMOVAL OF CONTAMINANTS BY PASSIVE TREATMENT SYSTEMS

Chapter 2 described chemical and biological processes that decrease concentrations of mine water contaminants in aquatic environments. The successful utilization of these processes in a mine water treatment system depends, however, on their kinetics. Chemical treatment systems function by creating chemical environments where metal removal processes are very rapid. The rates of chemical and biological processes that underlie passive systems are often slower than their chemical system counterparts and thus require that mine water be retained longer before it can be discharged. Retention time is gained by building large systems such as wetlands. Because the land area available for wetlands on minesites is often limited, the sizing of passive treatment systems is a crucial aspect of their design. Unfortunately, in the past, most passive treatment systems have been sized based on guidelines that ignored water chemistry or on available space, rather than on comparisons of contaminant production by the mine water discharge and expected contaminant removal by the treatment system. Given the absence of quantitative sizing standards, wetlands have been constructed that are both vastly undersized and oversized.

In this chapter, rates of contaminated removal are described for 13 passive treatment systems in western Pennsylvania. The systems were selected to represent the wide diversity of mine water chemical compositions that exist in the eastern United States. The rates that are reported from these sites are the basis of treatment system sizing criteria suggested in chapter 4.

The analytical approach used to quantify the performance of passive treatment systems in this chapter differs from the approach used by other researchers in several respects. First, contaminant removal is evaluated from a rate perspective, not a concentration perspective. Second, changes in contaminant concentrations are partitioned into two components: because of dilution from inputs of freshwater, and because of chemical and biological processes in the wetland. In the evaluations of wetland performance, only the chemical and biological components are considered. Third, treatment systems, or portions of systems, were included in the case studies only if contaminant concentrations were high enough to ensure that contaminant removal rates were not limited by the absence of the contaminant. These unique aspects of the research are discussed in further detail below.

EVALUATION OF TREATMENT SYSTEM PERFORMANCE

To make reliable evaluations of wetland performance, a measure should be used that allows comparison of contaminant removal between systems that vary in size and the chemical composition and flow rate of mine water they receive. In the past, concentration efficiency (CE%) has been a common measure of performance (*11-12*). Using iron concentration as an example, the calculation is

$$CE\% = \frac{Fe_{in} - Fe_{eff}}{Fe_{in}} \times 100 \qquad (2)$$

where the subscripts "in" and "eff" represent wetland influent and effluent sampling stations and Fe concentrations are in milligram per liter.

Except in carefully controlled environments, CE% is a very poor measure of wetland performance. The efficiency calculation results in the same measure of performance for a system that lowers Fe concentrations from 300 to 100 $mg \cdot L^{-1}$ as one that lowers concentrations from 3 to 1 $mg \cdot L^{-1}$. Neither the flow rate of the drainage nor the size of the treatment system are incorporated into the calculation. As a result, the performances of systems have been compared without accounting for differences in flow rate (which vary from <10 to >1000 $L \cdot min^{-1}$) or for differences in system size (which vary from <0.1 to >10 ha) (*12*).

A more appropriate method for measuring the performance of treatment systems calculates contaminant removal from a loading perspective. The daily load of contaminant received by a wetland is calculated from the product of concentration and flow rate data. For Fe, the calculation is

$$Fe\ (g \cdot d^{-1})_{in} = 1.44 \times flow\ (L \cdot min^{-1}) \times Fe\ (mg \cdot L^{-1})_{in}) \qquad (3)$$

where $g \cdot d^{-1}$ is gram per day and 1.44 is the unit conversion factor needed to convert minutes to days and milligrams to grams.

The contaminant load is apportioned to the down flow treatment system by dividing by a measure of the system's size. In this study, treatment systems are sized based on their surface area (SA) measured in square meter,

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{in} = Fe\ (g \cdot d^{-1})_{in} / SA. \qquad (4)$$

The daily mass of Fe removed by the wetland between two sampling stations, $Fe(g \cdot d^{-1})_{rem}$, is calculated by comparing contaminant loadings at the two points,

$$Fe\ (g \cdot d^{-1})_{rem} = (Fe\ g \cdot d^{-1})_{in} - (Fe\ g \cdot d^{-1})_{eff}. \qquad (5)$$

An area-adjusted daily Fe removal rate is then calculated by dividing the load removed by the surface area of the treatment system lying between the sampling points,

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{rem} = Fe\ (g \cdot d^{-1})_{rem} / SA. \qquad (6)$$

To illustrate the use of contaminant loading and contaminant removal calculations, consider the hypothetical water quality data presented in table 9.

In systems A and B, changes in Fe concentrations are the same (60 $mg \cdot L^{-1}$), but because system B receives four times more flow and thus higher Fe loading, it actually removes four times more Fe from the water. The concentration efficiencies of the two wetlands are equivalent, but the masses of Fe removed are quite different.

Data are shown for system C for three sampling dates on which flow rates and influent iron concentrations vary. On the first date (C1), the wetland removes all of the Fe that it receives. On the next two dates (C2 and C3), Fe loadings are higher and the wetland effluent contains Fe. From an efficiency standpoint, performance is best on the first date and is worst on the third date. From an Fe-removal perspective, the system is removing the least amount of Fe on the first date. On the second and third dates, the wetland removes similar amounts of iron (2,880 and 3,024 $g \cdot d^{-1}$). Variation in effluent chemistry results, not from changes in wetland's Fe-removal performance, but from variation in influent Fe loading.

Table 9.—Hypothetical wetland data and performance evaluations

System	Wetland size, m^2	Flow rate $L \cdot min^{-1}$	Fe Concentration In $mg \cdot L^{-1}$	Fe Concentration Eff $mg \cdot L^{-1}$	Fe Loading In $Kg \cdot d^{-1}$	Fe Loading Eff $Kg \cdot d^{-1}$	Fe removal performance CE %	Fe removal performance Rate $g \cdot m^{-2} \cdot d^{-1}$
A	400	10	100	40	1.4	0.6	60	2.2
B	400	40	100	40	5.8	2.3	60	8.6
C1	500	30	40	<1	1.7	<0.1	99	3.5
C2	500	80	35	10	4.0	1.2	71	5.8
C3	500	150	30	16	6.5	3.5	47	6.0
D	750	50	100	25	7.2	1.8	75	7.2

In Influent.
Eff Effluent.
CE Concentration efficiency.

Lastly, consider a comparison of wetland systems of different sizes. System D removes more iron than any wetland considered (5,400 $g \cdot d^{-1}$), but it is also larger. One would expect that, all other factors being equal, the largest wetland would remove the most Fe. When wetland area is incorporated into the measure by calculating area-adjusted Fe removal rates (gram per square meter per day), System B emerges as the most efficient wetland considered.

DILUTION ADJUSTMENTS

Contaminant concentrations decrease as water flows through treatment systems because chemical and biological processes remove contaminants from solution and because the concentrations are diluted by inputs of freshwater. To recognize and quantify the removal of contaminants by biological and chemical processes in passive treatment systems, it is necessary to remove the effects of dilution. Ideally, studies of treatment systems include the development of detailed hydrologic and chemical budgets so that dilution effects are readily apparent. In practice, the hydrologic information needed to develop these budgets is rarely available, except when systems are built for research purposes. Treatment systems constructed by mining companies and reclamation groups are rarely designed to facilitate flow measurements at all water sampling locations, so estimating dilution from hydrologic information is highly inaccurate or impossible.

An alternative method for distinguishing the effects of dilution from those of chemical and biological processes is through the use of a conservative ion (*44-45*). By definition, the concentration of a conservative ion changes between two sampling points only because of dilution or evaporation. Changes in concentrations of contaminant ions that proportionately exceed those of conservative ions can then be attributed to biological and chemical wetland processes.

In this study, Mg was used as a conservative ion. Magnesium was considered a good indicator of dilution in these systems for both theoretical and empirical reasons. In northern Appalachia, concentrations of Mg in coal mine drainage are often >50 $mg \cdot L^{-1}$, while concentrations in rainfall are <1 $mg \cdot L^{-1}$ and in surface runoff are usually <5 $mg \cdot L^{-1}$. Magnesium is unlikely to precipitate in passive treatment systems because the potential solid precipitates, $MgSO_4$, $MgCO_3$, and $CaMg(CO_3)_2$, do not form at the concentrations and pH conditions found in the systems (*23*). While biological and soil processes exist that may remove Mg in wetlands, their significance is negligible relative to the high Mg loadings that most mine water treatment systems in northern Appalachia receive. The average Mg loading for wetland systems included in this study was ~7,000 g $Mg \cdot m^{-2} \cdot yr^{-1}$. The uptake of dissolved Mg by plants in constructed wetlands can only account for 5 to 10 g $Mg \cdot m^{-2} \cdot yr^{-1}$. This estimate assumes that the net primary productivity of the constructed wetlands is 2,000 $g \cdot m^{-2} \cdot yr^{-1}$ dry weight (*46*) and that the Mg content of this biomass is 0.25% to 0.50% (*47*). The estimate ignores mineralization processes that would decrease the net retention of Mg to lower values. Most constructed wetlands have a clay base that can adsorb Mg by cation exchange processes, but the total removal of Mg by this process is limited to about 100 $g \cdot m^{-2}$. This estimate assumes that the mine water is in contact with a 5-cm-deep clay substrate that has a density of 1.5 $g \cdot cm^{-3}$, a cation exchange capacity of 25 meq per 100 g, and 50% of the available sites are occupied by Mg (*48*). These conservative calculations indicate that less than 2% of the annual Mg loading at the study sites is likely affected by biological and soil processes within the systems.

Empirical data also indicate that Mg is conservative in the wetlands monitored in this study. Table 10 shows influent and effluent concentrations of major noncontaminant ions at eight constructed wetlands. No precipitation had occurred in the study area for 2 weeks previous to collection of the samples, so dilution from rainfall, surface water, or shallow ground water seeps was minimal. Magnesium was the most conservative ion measured. Concentrations of Mg changed by <5% with flow through every wetland, while concentrations of all other ions monitored changed by at least 15% at at least one site.

Table 10.—Influent and effluent concentrations of Ca, Mg, Na, and sulfate at eight constructed wetlands

	Ca			Mg			Na			SO_4		
	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %
Donegal	244	241	-1	81	79	-2	6	6	0	729	729	0
Emlenton	429	433	+1	308	306	-1	11	10	-2	2,810	2,770	-1
FH	122	189	+55	51	51	0	5	7	+2	1,125	842	-25
Gourley	117	120	+3	114	117	+3	3	4	+6	1,000	1,030	+3
Latrobe	244	256	+14	127	125	-2	6	11	+8	1,525	1,225	-20
Piney A	416	426	+2	251	262	+4	15	16	+4	2,190	2,120	-3
Piney B	355	354	0	217	216	0	27	27	-2	2,050	2,100	+2
Somerset	307	469	+53	312	312	0	6	7	+15	2,740	2,300	-16

Eff Effluent.
In Influent.
FH Friendship Hill National Historical Site.

Changes in concentrations of Mg were used to adjust for dilution effects by the following method. For each set of water samples from a constructed wetland, a dilution factor (DF) was calculated from changes in concentrations of Mg between the influent and effluent station:

$$DF = Mg_{eff} / Mg_{in} . \quad (7)$$

Contaminant concentrations were adjusted to account for dilution using the DF. When only an influent flow rate was available, the chemical composition of the effluent water sample was adjusted. For Fe, the adjustment calculation was

$$\Delta Fe_{DA} = Fe_{in} - (Fe_{eff} / DF) \quad (8)$$

where ΔFe_{DA} is expressed in milligram per liter. When only an effluent flow rate was available, the chemical composition of the influent water sample was adjusted,

$$\Delta Fe_{DA} = (Fe_{in} \times DF) - Fe_{eff} . \quad (9)$$

Because most of the DF values were <1.00, the adjustment procedures generally resulted in smaller estimates of changes in contaminant concentrations than would have been calculated without the dilution adjustment.

Rates of contaminant removal, expressed as gram per square meter per day, were then calculated from the dilution-adjusted change in concentrations, the flow rate measurement liter per minute, and the SA of the system, in square meter

$$Fe(g \cdot m^{-2} \cdot day^{-1})_{rem} = (\Delta Fe_{DA} \times Flow \times 1.44)/SA . \quad (10)$$

LOADING LIMITATIONS

A primary purpose of this chapter is to define the contaminant removal capabilities of passive treatment systems. Accurate assessments of these capabilities require that the treatment systems studied contain excessive concentrations of the contaminants. A system that is completely effective (lowers a contaminant to <2 $mg \cdot L^{-1}$) may provide an indication that contaminant removal occurs (if dilution is not the cause of concentration changes), but cannot provide an estimate of the capabilities of the removal processes, as the rate of contaminant removal may be limited simply by the contaminant loading rate. For example, in table 9, the removal rate of Fe for wetland C1 is 3.5 $g \cdot m^{-2} \cdot d^{-1}$. This rate is not an accurate estimate of the capability of the wetland to remove Fe because the loading rate on this day was also only 3.5 $g \cdot m^{-2} \cdot d^{-1}$. The data from C1 are not sufficient to estimate whether the wetland could have removed 10 or 100 $g \cdot m^{-2} \cdot d^{-1}$ of Fe. Only when the wetland is overloaded with Fe (days C2 and C3), can the Fe removal capabilities of the wetland be assessed.

The Morrison passive treatment system demonstrates the necessity of recognizing both dilution and loading-limiting situations in the evaluation of the kinetics of metal removal processes. The Morrison system consists of an anoxic limestone drain followed by a ditch, a settling pond, and two wetland cells. Figure 5, previously presented in chapter 2, shows average concentrations of Fe, Mn, and Mg at the sampling stations. Iron loading and removal rates for the sampling stations are shown in table 11. The treatment system decreased concentrations of Fe from 151 $mg \cdot L^{-1}$ at the system influent station (the ALD discharge) to <1 $mg \cdot L^{-1}$ at the final wetland effluent station. Most of the change in Fe chemistry occurred in the ditch, a portion of the system that only accounted for 4% of the total treatment system SA. Calculations of the rate of Fe removal based on the entire treatment system resulted in a value of 1.3 $g \cdot m^{-2} \cdot d^{-1}$. Because this removal rate is equivalent to the load, it does not represent a reliable approximation of the system's Fe-removal capablity. Only when an Fe removal rate is calculated for the ditch, an area where Fe loading exceeded Fe removal, does an accurate assessment of the Fe removal capabilities result.

Table 11.—Average concentrations of Fe, Mn, and Mg at the Morrison passive treatment system

Station	Cumulative area, m^2	Flow, $L \cdot m^{-1}$	Concentration, $mg \cdot L^{-1}$			Removal rate[1], $g \cdot m^{-2} \cdot d^{-1}$	
			Fe	Mn	Mg	Fe	Mn
Influent	0	6.6	151	42	102	NA	NA
Ditch Effluent	43	NA	56	37	91	19.2	0.17
Pond Effluent	461	NA	5	24	72	2.3	0.14
Final Effluent	1,076	NA	<1	71	71	1.3	0.13

NA Not available.

[1]Removal rate based on cumulative area.

Concentrations of Mn at the Morrison effluent station were generally above discharge limits. Manganese was detectable in every effluent water sample (>.4 mg•L^{-1}) and >2 mg•L^{-1} in 75% of the samples. Thus, it was reasonable to evaluate the kinetics of Mn removal based on the SA of the entire treatment system. Concentrations of Mg, however, decreased with flow through the treatment system, suggesting an important dilution component. Effluent water samples contained, on average, 31% lower concentrations of Mg than did the influent samples. On several occassions when the site was sampled in conjunction with a rainstorm, differences between effluent and influent concentrations of Mg were larger than 50%. Measurements of metal removal by the Morrision treatment system that did not attempt to account for dilution would significantly overestimate the actual kinetics of metal removal processes.

Dilution adjustments were possible for every set of water samples collected from a treatment system because concentrations of Mg were determined for every water sample. Problems with loading limitations, however, could not be corrected at every site. At two sites where complete removal of Fe occurred, the Blair and Donegal wetlands, the designs of the systems were not conducive for the establishment of intermediate sampling stations. For these two systems, no Fe removal rates were calculated because complete removal of Fe occurred over an undetermined area of treatment system.

STUDY SITES

The design characteristics of the 13 passive treatment systems monitored during this study are shown in table 12. At four of the sites, acidic mine water was pretreated with anoxic limestone drains (ALD's) before it flowed into constructed wetlands. The construction materials for the wetlands ranged from mineral substances, such as clay and limestone rocks, to organic substances such as spent mushroom compost, manure, and hay bales. Cattails (*Typha latifolia* and, less commonly, *T. angustifolia*) were the most common emergent plants growing in the systems. Three sites contained few emergent plants. Most of the wetland systems consisted of several cells or ponds connected serially. Two systems, however, each consisted of a single long ditch.

The mean influent flow rates of mine drainage at the study sites ranged from 7 to 8,600 L•min^{-1} (table 12). The highest flow rates occurred where drainage discharged from abandoned and flooded underground mines. The lowest flow rates occurred at surface mining sites. Estimated average retention times ranged from 8 h to more than 30 days.

The average chemistry of the influents to the 16 constructed wetlands are shown in table 13. Data from 15 sampling points are shown. At the REM site, two discharges are treated by distinct ALD-wetland systems that eventually merge into a single flow. The combined flows are referred to as REM-Lower. Mine water at the Howe Bridge system is characterized at two locations. The "upper" analysis describes mine water discharging from an ALD that flows into aerobic settling ponds. The "lower" analysis describes the chemistry of water flowing out of the last settling pond and into a large compost-limestone wetland that is constructed so that mine water flows in a subsurface manner.

Table 12.—Construction characteristics of the constructed wetlands

Site	Constructed year	Design	Substrate	Emergent vegetation	SA, m^2	Water depth, cm	Flow rate,[1] L•min^{-1}	Est. ret. time,[2] days
Donegal	1987	Pond, 8 Cells	LS, SMC	*Typha*	8,100	15	501	1.7
Cedar	1989	5 Cells	Clay, LS	.. do.	1,360	15	156	0.9
Keystone	1989	Ditch	Topsoil	None	4,200	100	8,606	.3
Blair	1989	Ditch	Manure, straw	Mixed	1,080	5	11	3.4
Shade	1989	ALD, 2 Cells	LS	None	880	10	10	6.4
Piney	1987	1 Cell	HB	Mixed	2,500	50	468	1.9
Morrison	1990	ALD, 3 Cells	Clay, manure	*Typha*	1,075	30	7	33.9
Emlenton	1987	9 Cells	LS, manure	.. do.	643	50	55	4.1
Somerset	1984	2 Cells	HB, LS, SMC	.. do.	1,005	15	47	2.2
Howe	1991	ALD, 3 Cells	Clay, LS, SMC	None	3,000	50	130	8.0
Latrobe	1987	3 Cells	HB, LS, SMC	*Typha*	2,800	15	86	3.4
REM	1992	2 ALDs, 9 Cells	SMC	.. do.	4,849	30	206	4.9
FH	1988	6 Cells	LS, SMC	.. do.	667	15	15	4.6

Est. Estimated.
FH Friendship Hill National Historical Site.
HB Haybales.
LS Limestone.
ret. Retention.
SA Surface area of wet area.
SMC Spent mushroom compost.
[1] Average values.
[2] Calculated from the water holding capacity and influent flow rate.

Table 13.—Average chemical characteristics of influent water at the constructed wetlands (sites are arranged according to the net acidity)

Site	Number of samples	pH	Composition, mg•L^{-1}						Net Acidity,[1,2] mg•L^{-1}
			Alk	Fe	Mn	Al	Mg	SO_4	
Donegal	29	7.1	202	5	8	<1	81	738	-182
Cedar	26	6.3	336	92	2	<1	54	1,251	-140
Keystone	28	6.3	142	37	<1	<1	14	330	-73
Blair	12	6.2	166	52	30	<1	77	645	-51
Shade	20	6.0	31	<2	22	<1	125	966	-17
Piney	39	5.8	60	1	15	<1	225	1,845	-6
Morrison	34	6.3	271	150	42	<1	102	1,087	75
REM - L	20	6.1	128	190	50	<1	118	1,275	258
Howe - Lower	13	5.6	22	185	34	<1	91	1,128	312
Emlenton	40	4.7	15	89	77	8	249	2,317	320
Somerset	43	4.4	0	162	50	3	193	1,691	373
Howe - Upper	13	6.2	160	272	39	<1	105	1,315	375
REM-Lower	9	3.5	0	246	92	2	171	1,875	496
Latrobe	43	3.5	0	125	32	43	125	1,655	617
REM - R	18	5.5	57	473	130	3	232	2,495	867
FH	73	2.6	0	153	9	58	85	1,733	929

Alk Alkalinity.
FH Friendship Hill National Historical Site.
[1]$CaCO_3$ equivalent.
[2]Negative values indicate alkaline conditions.

Ten of the influents to the constructed wetlands had pH >5 and concentrations of alkalinity >25 mg•L^{-1}. The alkaline character of five of these discharges resulted from pretreatment of the mine water with ALD's. The high concentrations of alkalinity contained by five discharges not pretreated with ALD's arose from natural geochemical reactions within the mine spoil (Donegal and Blair) or the flooded deep mine (Cedar, Keystone, and Piney). For mine waters that contained appreciable alkalinity, the principal contaminants were Fe and Mn.

Concentrations of alkalinity for six of the influents were high enough to result in a net alkaline conditions (negative net acidity in table 13). A seventh alkaline influent, Morrison, was only slightly net acidic. For these seven influents, enough alkalinity existed in the mine waters to offset the mineral acidity associated with Fe oxidation and hydrolysis.

Nine of the influents were highly acidic. Five of the acidic influents contained alkalinity, but mineral acidity associated with dissolved Fe and Mn caused the solutions to be highly net acidic. These inadequately buffered waters were contaminated with Fe and Mn. Four of the waters contained no appreciable alkalinity (pH <4.5) and high concentrations of acidity. Mine waters with low pH were contaminated with Fe, Mn, and Al.

EFFECTS OF TREATMENT SYSTEMS ON CONTAMINANT CONCENTRATIONS

The effects of the treatment systems on contaminant concentrations are shown in table 14. Every system decreased concentrations of Fe. At four sites where the original mine discharge contained elevated concentrations of Fe, the final discharges contained <1 mg•L^{-1}. Nine of the systems decreased Fe concentrations by more than 50 mg•L^{-1}. The largest change in Fe occurred at the Howe Bridge system where concentrations decreased by 197 mg•L^{-1}. From a compliance perspective, the most impressive decrease in Fe occurred at the Morrison system where 151 mg•L^{-1} decreased to <1 mg•L^{-1}.

Fourteen of the passive systems received mine water contaminated with Mn. Eleven of these systems decreased concentrations of Mn. Changes in Mn were smaller than changes in Fe. The largest change in Mn concentration, 31 mg•L^{-1}, occurred at the Morrison site. Only the Donegal treatment system discharged water that consistently met effluent criteria for Mn (<2 mg•L^{-1}). Both the Shade and Blair wetland effluents flowed into settling ponds which discharged water in compliance with regulatory criteria. On occassions, the discharges of the Morrison and Piney treatment systems met compliance criteria.

Every wetland system decreased concentrations of acidity. The Morrison system, which received mine water that contained 75 mg•L^{-1} acidity, always discharged net alkaline water. None of the constructed wetlands that received highly acidic water (net acidity >100 mg•L^{-1}) regularly discharged water with a net alkalinity. During low-flow periods, the Somerset, Latrobe, and FH systems discharged net alkaline water. The largest change in acidity occurred at the Somerset wetland where concentrations decreased by an average 304 mg•L^{-1}.

DILUTION FACTORS

While contaminant concentrations decreased with flow through every constructed wetland, concentrations of Mg also decreased at many of the sites. Decreases in Mg

indicated that part of the improvement in water quality was because of dilution. Average dilution factors for the treatment systems are shown in table 15. For 9 of the 17 systems, average dilution factors were 0.95 to 1.00 and dilution adjustments were minor. At the remaining eight systems, mean DF values were less than 0.95 and dilution adjustments averaged more than 5%. Water quality data from the Morrison and Somerset constructed wetlands were adjusted, on average, by more than 25%.

Dilution factors varied widely between sampling days. Dilution adjustments were higher for pairs of samples collected in conjuction with precipitation events or thaws. Every system was adjusted by more than 5% on at least one occassion (see minimum dilution factors in table 15). Adjustments of more than 20% occurred on at least one occasion at 13 of the 17 study sites.

Few dilution adjustments were >1.00 (see maximum dilution factors in table 15). Of the 390 dilution factors that were calculated for the entire data set, 13 exceeded 1.05. These high dilution factors could have resulted from evaporation or freezing out of uncontaminated water within the treatment system, from temporal changes in water chemistry, or from sampling errors. Most of the high dilution factors were associated with rainstorm events, suggesting temporal changes in water quality. When dilution factors were >1.00, the calculated rates of contaminant removal were greater than would have been estimated without any dilution adjustment. Because of the limited number of sample pairs with high dilution factors, their presence did not markedly affect the average contaminant removal rates for the constructed wetland study areas.

Table 14.—Mean water quality for sampling stations at the constructed wetlands

Site	Sampling station	n[1]	pH	Fe	Mn	Acidity	Mg
Donegal	Pond influent	6	6.4	34	9	NAp	83
	Wetland influent	29	7.1	5	8	NAp	81
	Effluent	28	7.4	<1	2	NAp	80
Cedar	Influent	26	6.3	92	2	NAp	54
	Effluent	27	6.4	41	2	NAp	53
Keystone	Influent	28	6.3	37	1	NAp	14
	Effluent	28	6.4	32	1	NAp	14
Blair	Influent	12	6.2	52	30	NAp	77
	Effluent	8	7.0	<1	5	NAp	59
Shade	LC influent	20	6.0	2	23	NAp	128
	LC effluent	20	6.8	<1	10	NAp	122
Piney	Seep	21	5.4	32	25	NAp	201
	Wetland influent	39	5.8	1	15	NAp	225
	Wetland effluent	39	6.1	<1	11	NAp	225
Morrison	Influent	24	6.3	151	42	75	102
	Ditch	24	6.4	56	37	64	91
	Effluent	24	6.6	<1	11	-1	71
REM-L	Left influent	20	6.1	190	50	258	118
	Left effluent	20	3.8	84	48	225	112
Emlenton	Influent	46	4.7	89	77	320	249
	Effluent	40	3.2	15	73	271	234
Somerset	Influent	43	4.4	162	50	373	193
	Effluent	40	5.5	18	33	69	139
Howe	Influents[2]	13	6.0	265	37	373	101
	Upper effluent	13	5.6	185	34	312	91
	Lower effluent	13	6.2	68	33	112	91
REM-Lower	Influent	9	3.5	246	92	496	171
	Effluent	9	2.9	115	88	436	166
Latrobe	Influent	43	3.5	125	32	617	125
	Cell 3 effluent	43	3.7	56	29	343	122
REM-R	Right influent	18	5.5	473	130	867	232
	Right effluent	18	3.3	338	113	712	201
FH	Influent	73	2.6	153	10	929	85
	Effluent	73	2.9	137	10	674	85

FH Friendship Hill National Historical Site.
LC Limestone cell.
NAp Not applicable.
[1]Number of samples.
[2]The flow-weighted average of two discharges.

Table 15.—Dilution factors for the constructed wetlands

Site	Average	sd	Minimum	Maximum
Donegal	0.99	0.05	0.76	1.04
Cedar	0.99	0.03	0.92	1.05
Keystone	0.99	0.04	0.91	1.15
Blair	0.83	0.10	0.70	1.01
Shade	0.96	0.08	0.76	1.09
Piney	1.00	0.06	0.92	1.31
Morrison Ditch ..	0.87	0.18	0.40	1.05
Morrison Wetland	0.69	0.25	0.27	1.12
REM-L	0.95	0.09	0.70	1.13
Howe Lower	1.00	0.10	0.80	1.25
Emlenton	0.94	0.09	0.66	1.04
Somerset	0.73	0.30	0.30	1.76
Howe Upper	0.89	0.08	0.73	0.99
REM-Lower	0.93	0.09	0.72	1.01
Latrobe	0.95	0.08	0.75	1.14
REM-R	0.86	0.16	0.36	1.00
FH	1.00	0.12	0.58	1.34

FH Friendship Hill National Historical Site.

REMOVAL OF METALS FROM ALKALINE MINE WATER

Rates of Fe and Mn removal for the study systems are shown in table 16. Significant removal of Fe occurred at every study site. Fe removal rates were directly correlated with pH and the presence of bicarbonate alkalinity (figure 9). These two water quality parameters are closely related because the buffering effect of bicarbonate alkalinity causes mine waters with >50 mg•L alkalinity to typically have a pH between 6.0 and 6.5. Within the group of sites that received alkaline mine water, there was not a significant relationship between the Fe removal rate and the concentration of alkalinity.

Removal of Fe at the alkaline mine water sites appeared to occur principly through the oxidation of ferrous iron and the precipitation of ferric hydroxide (reaction A, chapter 2). Mine water within the systems was turbid with suspended ferric hydroxides. By the cessation of the studies, each of the alkaline water sites had developed thick accumulations of iron oxyhydroxides. Laboratory experiments, discussed in chapter 2, demonstrated that abiotic ferrous iron oxidation processes are rapid in aerated alkaline mine waters. No evidence was found that microbially-mediated anaerobic Fe removal processes, which require the presence of an organic substrate, contributed significantly to Fe removal at the alkaline sites. Fe removal rates at the REM wetlands, which were constructed with fertile compost substrates, did not differ from rates at sites constructed with mineral substrates (Morrison, Howe-Upper, Keystone).

Rates of Fe removal averaged 23 $g \cdot m^{-2} \cdot d^{-1}$ at the six sites that contained alkaline, Fe-contaminated water. Four of the alkaline systems displayed similar rates despite widely varying flow conditions, water chemistry and system designs. The Keystone system, a deep plantless ditch that lowered Fe concentrations in a very large deep mine discharge by 5 mg L^{-1}, removed Fe at a rate of 21 $g \cdot m^{-2} \cdot d^{-1}$. The shallow-water Morrison ditch, which decreased concentrations of Fe in a low-flow seep by almost 100 $mg \cdot L^{-1}$, had an average Fe removal rate of 19 $g \cdot m^{-2} \cdot d^{-1}$. The REM-L and REM-R wetlands, which were constructed almost identically, but received water with contaminant concentrations and flow rates that varied by 200%, displayed Fe removal rates of 20 and 28 $g \cdot m^{-2} \cdot d^{-1}$.

Table 16.—Fe and Mn removal rates at constructed wetland

Site	Fe removal rate				Mn removal rate			
	Mean	Std dev	n	sig?[1]	Mean	Std dev	n	sig?
Donegal	NAp	NAp	NAp	NAp	0.50	0.25	9	yes
Cedar	6.3	2.2	7	yes	0.17	0.41	7	no
Keystone	20.7	5.1	15	yes	NAp	NAp	NAp	NAp
Blair	NAp	NAp	NAp	NAp	0.43	0.37	6	yes
Shade	NAp	NAp	NAp	NAp	0.72	0.64	17	yes
Piney	NAp	NAp	NAp	NAp	1.07	1.34	33	yes
Morrison Dit	19.2	10.6	24	yes	0.17	0.41	24	yes
Morrison Wet	NAp	NAp	NAp	NAp	0.20	0.18	24	yes
REM-L	28.3	5.7	20	yes	-0.05	0.13	20	no
Howe-Lower	8.1	1.9	13	yes	0.06	0.16	13	no
Emlenton	9.1	3.3	39	yes	-0.09	0.19	39	no
Somerset	5.0	4.9	34	yes	-0.01	0.54	34	no
Howe-Upper	42.7	8.2	13	yes	-0.43	0.49	13	no
REM-Lower	12.0	3.4	9	yes	-0.05	0.14	9	no
Latrobe	2.1	1.0	21	yes	0.03	0.09	21	no
REM-R	20.1	4.0	18	yes	0.10	0.33	18	no
FH	0.5	0.5	73	yes	0.00	0.02	73	no

NAp Not applicable.
FH Friendship Hill National Historical Site.
n Sample size.
sig? Significant at 0.05 level.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

Two alkaline mine water sites varied considerably from the other sites in their Fe removal capabilities. The Cedar Grove wetland removed Fe at a rate of 6 $g \cdot m^{-2} \cdot d^{-1}$, while the Howe Bridge Upper site removed Fe at a rate of 43 $g \cdot m^{-2} \cdot d^{-1}$. The Cedar Grove system consists of a series of square cells that may have more short-circuiting flow paths than the rectangular-shaped cells of the other systems. The Cedar Grove system also contains less aeration structures than the other systems. Mine water at the site upwells from a flooded underground mine into a pond that dicharges into a three-cell wetland. Limited topographic relief prevented the inclusion of structures that efficiently aerate the water (i.e., waterfalls, steps). The Howe Bridge Upper system, in contrast, very effectively aerates water. Drainage drops out of a 0.3-m-high pipe, flows down a cascading ditch and through a V-notch weir before it enters a large settling pond. Because the rate of abiotic ferrous iron oxidation is directly proportional to the concentration of dissolved oxygen, insufficient oxygen transfer may explain the low rate of Fe removal at the Cedar Site, while exceptionally good oxygen transfer at the Howe Bridge Upper site may explain its high rate of Fe removal.

At sites where the buffering capacity of bicarbonate alkalinity exceeded the mineral acidity associated with iron hydrolysis, precipitation of Fe did not result in decreased pH. This neutralization was evident at the Morrison, Cedar, Keystone, Blair, Piney, and Donegal sites (table 14). At the Howe Bridge and REM wetlands, the mine water was insufficiently buffered and iron hydrolysis eventually exhausted the alkalinity and pH fell to low levels. The effluents of both REM systems had pH <3.5. The Howe Bridge Upper system discharged marginally alkaline water (<25 $mg \cdot L^{-1}$ alkalinity; pH 5.6). Spot checks of the pH of surface water 20 m into the Howe Bridge Lower wetland (which receives the Upper system effluent) always indicated pH values <3.5.

Significant removal of Mn only occurred at five of the constructed wetlands (table 13). Each of these sites received alkaline mine water (figure 10). Each site also either received water with low concentrations of Fe (Piney and Shade) or developed low concentrations of Fe within the treatment system (Blair, Donegal, and Morrison).

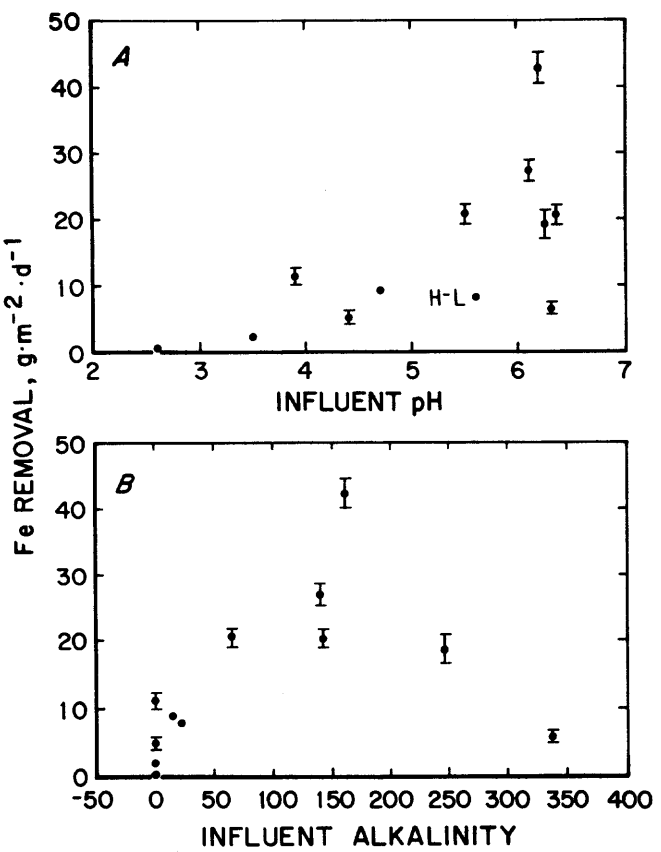

Figure 9.—Relationship between mean Fe removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below the mean. "H-L" is the Howe-Lower site.

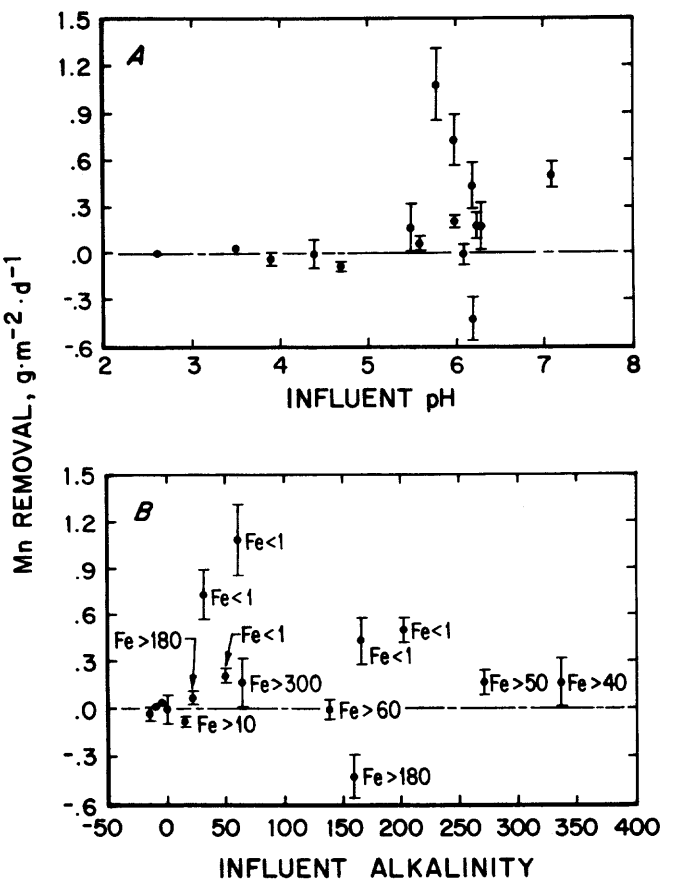

Figure 10.—Relationship between mean Mn removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below mean. Fe values next to the bars are effluent Fe^{2+} values.

Alkaline sites that contained high concentrations of Fe throughout the treatment system (Howe-Upper, REM-L, REM-R, and Cedar), did not remove significant amounts of Mn. The Morrison ditch, which contained water with an average 56 $mg \cdot L^{-1}$ Fe, had a significant Mn removal rate. This rate, however, was derived from an average dilution-adjusted decrease in Mn concentrations of only 1.2 $mg \cdot L^{-1}$ or 3% of the influent concentrations. Because of uncertainities with sampling, analysis, and dilution-adjustment procedures that could reasonably bias Mn data by 2-3%, the authors do not currently place much practical confidence in this value.

The five sites that markedly decreased concentrations of Mn had variable designs. The Donegal wetland has a thick organic and limestone substrate and is densely vegetated with cattails. The Blair and Morrison wetlands contain manure substrates and are densely vegetated with emergent vegetation. The Piney wetland was not constructed with an organic substrate and includes deep open water areas and shallow vegetated areas. The Shade treatment system contains limestone rocks, no organic substrate, and few emergent plants. Thus, chemical aspects of the water, not particular design parameters, appear to principally control Mn removal in constructed wetlands.

The removal of Mn from aerobic mine waters appeared to result from oxidation and hydrolysis processes. Black Mn-rich sediments were visually abundant in the Shade, Donegal, and Blair wetlands. As discussed in chapter 2, the specific mechanism by which these oxidized Mn solids form is unclear. The amorphous nature of the solids prevented identification by standard X-ray diffraction methods. However, samples of Mn-rich solids collected from the Shade and Blair wetlands were readily dissolved by alkaline ferrous iron solutions, indicating the presence of oxidized Mn compounds.

Mn^{2+} can reportedly be removed from water by its sorption to charged FeOOH (ferric oxydroxide) particles (*23, 30*). If this process is occurring at the study wetlands, it is not a significant sink for Mn removal. The bottoms of the Morrison ditch, Howe-Upper, Cedar, REM-L, and REM-R wetlands were covered with precipitated FeOOH and the mine water within these wetlands commonly contained 5 to 10 $mg \cdot L^{-1}$ of suspended FeOOH (difference of the Fe content of unfiltered and filtered water samples). After mine water concentrations were adjusted to reflect dilution, no removal of Mn was indicated at four of the sites and very minor removal of Mn occurred at the fifth site (Morrison ditch).

Although the processes that remove Mn and Fe from alkaline mine water appears to be mechanistically similar (both involve oxidation and hydrolysis reactions), the observed kinetics of the metal removal processes are quite different. In the alkaline mine waters studied, Mn removal rates were 20 to 40 times slower than Fe removal.

The presence or absence of emergent plants in the wetlands did not have a significant effect on rates of either Fe or Mn removal at the alkaline mine water sites. In general, bioaccumulation of metals in plant biomass is an insignificant component of Fe and Mn removal in constructed wetlands (*49*). The ability of emergent plants to oxygenate sediments and the water column (*50*) has been proposed as an important indirect plant function in wetlands constructed to treat polluted water (*51*). Either oxygenation of the water column is not a rate limiting aspect of metal oxidation at the constructed wetlands that received alkaline mine water, or physical oxygen transfer processes are more rapid than plant-induced processes.

REMOVAL OF METALS AND ACIDITY FROM ACID MINE DRAINAGE

Metal removal was slower at constructed wetlands that received acidic mine water than at those that received alkaline mine water. Removal of Mn did not occur at any site that received highly acidic water (figure 10). Removal of Fe occurred at every wetland that received acidic mine water, but the Fe removal rates were less than one-half those determined at alkaline wetlands (figure 9). Because abiotic ferrous iron oxidation processes are extremely slow at pH values <5, virtually all the Fe removal observed at the acidic sites must arise from direct or indirect microbial activity. Microbially-mediated Fe removal under acidic conditions is, however slower than abiotic Fe-removal processes under alkaline conditions.

Wetlands that treat acidic mine water must both precipitate metal contaminants and neutralize acidity. At most wetland sites, acidity neutralization was the slower process. At the Emlenton and REM wetlands, Fe removal processes were accompanied on every sampling occasion by an increase in proton acidity which markedly decreased pH (see figure 4*A*, chapter 2). Mine water pH occasionally decreased with flow through the Latrobe and Somerset wetlands. Thus, for the wetlands included in this study, the limiting aspect of acid mine water treatment was the generation of alkalinity or the removal of acidity (which were considered in this report to be equivalent, see chapter 2). The best measure of the effectiveness of the acid water treatment systems was through the calculation of acidity removal rates.

Acidity can be neutralized in wetlands through the alkalinity-producing processes of carbonate dissolution and bacterial sulfate reduction. As was discussed in chapter 2, the presence of an organic substrate where reduced Eh conditions develop promotes both alkalinity-generating processes. In highly reduced environments where dissolved oxygen and ferric iron are not present, carbonate surfaces are not passivated by FeOOH armoring. Decomposition of the organic substrate can result in elevated

partial pressures of CO_2 and promote carbonate dissolution. The presence of organic matter also promotes the activity of sulfate-reducing bacteria.

The rates of alkalinity generated from these two processes in the constructed wetlands were determined based on dilution-adjusted changes in the concentrations of dissolved Ca and sulfate, the stoichiometry of the alkalinity-generating reactions, and measured flow rates. The calculations are based on the assumption that Ca concentrations only increase because of carbonate dissolution and that sulfate concentrations only decrease because of bacterial sulfate reduction. One possible error in this approach is that sulfate can co-precipitate with ferric hydroxides in low-pH aerobic environments (*52*). The Fe and sulfate content of surface deposits collected from the constructed wetlands indicate that sulfate is incorporated into the precipitates collected from acidic environments at an average $Fe:SO_4$ ratio of 9.7 (table 17). If all of the Fe removed from mine water is assumed to precipitate as ferric hydroxide with a $Fe:SO_4$ ratio of 9.7:1, then changes in sulfate concentrations attributable to the co-precipitation process amount to only 5 to 30 $mg \cdot L^{-1}$ at the acid mine water sites. Dilution-adjusted changes in sulfate concentrations at the Somerset, Latrobe, Friendship Hill (FH), and Howe-Lower wetlands were commonly 200 to 500 $mg \cdot L^{-1}$.

Rates of acidity removal, sulfate removal and calcium addition for six constructed wetlands that received acidic mine water are shown in table 18. Significant removal of acidity occurred at all sites. The lowest rates of acidity removal occurred at the Emlenton wetland. This site consists of cattails growing in a manure and limestone substrate. No sulfate reduction was indicated (the rate was not significantly >0). Dissolution of the limestone was indicated, but the rate was the lowest observed.

Table 17.—Fe and SO_4 content of ferric oxyhydroxide deposits; sites are arranged by pH

Site	pH	Composition, ppm dry weight		
		Fe	SO_4	$Fe:SO_4$
Emlenton	3.0	471,779	64,213	7.4
Latrobe	3.5	288,939	27,991	10.3
Somerset	3.5	461,583	48,263	9.6
Cedar	6.4	362,300	8,946	40.5
Keystone	6.6	398,337	6,888	57.8

[1] Field pH measured where substrate sample collected.

The Latrobe, Somerset, FH, Howe-Lower, and REM systems were each constructed with a spent mushroom compost and limestone substrate. Spent mushroom compost is a good substrate for microbial growth and has a high limestone content (10% dry weight). At these five wetlands, sulfate reduction and limestone dissolution both occurred at significant rates (table 18). The summed amount of alkalinity generated by sulfate reduction and limestone dissolution processes (Reactions M and N, chapter 2) correlated strongly with the measured rate of acidity removal at these four sites (r >0.90 at each site). At the FH wetland, 94% of the measured acidity removal could be explained by these two processes (figure 11).

On average, sulfate reduction and limestone dissolution contributed equally to alkalinity generation at these five sites (51% versus 49%, respectively). The average sulfate removal rate calculated for the compost sites, 5.2 g $SO_4^{-2} \cdot m^{-2} \cdot d^{-1}$, is equivalent to a sulfate reduction rate of ~180 $nmol \cdot cm^{-3} \cdot d^{-1}$. This value is consistent with measurements of sulfate reduction made at the constructed wetlands using isotope methods (*41*) as well as measurements of sulfate reduction made for coastal ecosystems (*53*).

Table 18.—Average rates of acidity removal, sulfate removal, and calcium addition at sites receiving acidic mine water

Site	n	Acidity removal rate			Sulfate removal rate			Calcium addition rate		
		mean	Std dev	sig?[1]	mean	Std dev	sig?	mean	Std dev	sig?
Emlenton	25	3.1	2.4	yes	1.5	5.7	no	0.8	1.21	yes
Somerset	34	9.9	8.6	yes	5.1	5.7	yes	1.7	1.20	yes
Howe Lower	13	15.4	4.1	yes	8.9	7.2	yes	3.9	1.40	yes
REM-Lower	9	7.1	7.2	yes	2.9	2.4	yes	2.6	1.03	yes
Latrobe	21	6.9	4.4	yes	5.9	6.4	yes	0.9	0.07	yes
FH	72	7.0	3.8	yes	3.4	2.6	yes	1.2	0.80	yes

FH Friendship Hill National Historical Site.
n Sample size.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

The highest rates of acidity removal, sulfate reduction, and limestone dissolution all occurred at the Howe-Lower site. This system differs from the others by its subsurface flow system. Drainage pipes, buried in the limestone that underlies the compost, cause the mine water to flow directly through the substrate. At the Somerset, Latrobe, REM, and FH systems, water flows surficially through the wetlands. Mixing of the acidic surface water and alkaline substrate waters presumably occurs by diffusion processes at the surface-flow sites. By directly contacting contaminated water and alkaline substrate, the Howe-Lower site is extracting alkalinity from the substrate at a significantly higher rate than occurs in surface flow systems. How long the Howe-Upper system can continue to generate alkalinity at the present rates is unknown. Monitoring of the system, currently in its third year of operation, is continuing.

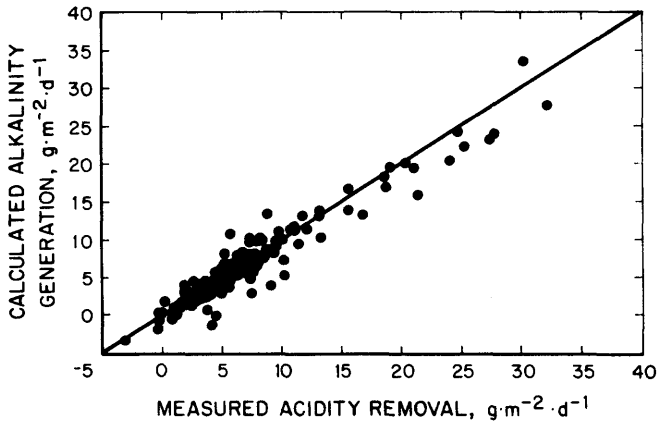

Figure 11.—Measured rates of alkalinity generation and acidity removal at the Friendship Hill wetland. Units are $g \cdot m^{-2} \cdot d^{-1}$ $CaCO_3$ equivalent.

CHAPTER 4. DESIGN AND SIZING OF PASSIVE TREATMENT SYSTEMS

Three principal types of passive technologies currently exist for the treatment of coal mine drainage: aerobic wetland systems, wetlands that contain an organic substrate, and anoxic limestone drains. In aerobic wetland systems, oxidation reactions occur and metals precipitate primarily as oxides and hydroxides. Most aerobic wetlands contain cattails growing in a clay or spoil substrate. However, plantless systems have also been constructed and at least in the case of alkaline influent water, function similarly to those containing plants (chapter 3).

Wetlands that contain an organic substrate are similar to aerobic wetlands in form, but also contain a thick layer of organic substrate. This substrate promotes chemical and microbial processes that generate alkalinity and neutralize acidic components of mine drainage. The term "compost wetland" is often used in this report to describe any constructed wetland that contains an organic substrate in which biological alkalinity-generating processes occur. Typical substrates used in these wetlands include spent mushroom compost, *Sphagnum* peat, haybales, and manure.

The ALD is a buried bed of limestone that is intended to add alkalinity to the mine water (*15, 33-34*). The limestone and mine water are kept anoxic so that dissolution can occur without armoring of limestone by ferric oxyhydroxides. ALD's are only intended to generate alkalinity, and must be followed by an aerobic system in which metals are removed through oxidation and hydrolysis reactions.

Each of the three passive technologies is most appropriate for a particular type of mine water problem. Often, they are most effectively used in combination with each other. In this chapter, a model is presented that is useful in deciding whether a mine water problem is suited to passive treatment, and also, in designing effective passive treatment systems.

Two sets of sizing criteria are provided (table 19). The "abandoned mined land (AML) criteria" are intended for groups that are attempting to cost-effectively decrease contaminant concentrations. In many AML situations, the goal is to improve water quality, not consistently achieve a specific effluent concentration. The AML sizing criteria are based on measurements of contaminant removal by existing constructed wetlands (chapter 3). Most of the removal rates were measured for treatment systems (or parts of treatment systems) that did not consistently lower concentrations of contaminants to compliance with OSM effluent standards. In particular, the Fe sizing factor for alkaline mine water (20 $g \cdot m^{-2} \cdot d^{-1}$) is based on data from six sites, only one of which lowers Fe concentrations to compliance.

Table 19.—Recommended sizing for passive treatment systems

	AML criteria, $g \cdot m^{-2} \cdot d^{-1}$		Compliance criteria, $g \cdot m^{-2} \cdot d^{-1}$	
	Alkaline	Acid	Alkaline	Acid
Fe	20	NAp	10	NAp
Mn	1.0	NAp	0.5	NAp
Acidity ..	NAp	7	NAp	3.5

NAp Not applicable.

It is possible that Fe removal rates are a function of Fe concentration; i.e., as concentrations get lower, the size of