DETERMINING THE CAPACITY FOR METAL RETENTION IN MAN-MADE WETLANDS CONSTRUCTED FOR TREATMENT OF COAL MINE DRAINAGE[1]

R. Kelman Wieder[2]

Abstract.--Within the past several years, there has been a tremendous increase in the use of man-made wetland systems for the treatment of acid coal mine drainage. However, quantitative estimates of the long-term capacity of a wetland for metal retention are lacking. In this paper, an upper limit for Fe retention in Sphagnum wetlands is estimated by individually considering the biological and chemical processes contributing to metal retention in wetland ecosystems. Also, different field monitoring schemes are discussed in terms of their potential for assessing the effectiveness of metal retention in man-made wetland systems and their potential for extrapolating the long-term capacity for effective treatment of mine drainage. Although it has been suggested that man-made wetlands may offer a low-cost approach to mine drainage treatment, cost/benefit analyses cannot be carried out without being able to reliably estimate long-term capacity for metal retention in a man-made wetland system given a particular volume and chemistry of mine drainage water. Until long-term capacity for metal retention in man-made wetlands can be reliably predicted, the environmental and economic potential of wetland treatment of coal mine drainage remains difficult to assess.

INTRODUCTION

One of the most frequently cited values of freshwater wetlands is their ability to act as nutrient sinks, improving the quality of water that flows through them (Greeson et al. 1978). This characteristic has been exploited in using freshwater wetlands for nitrogen and/or phosphorus removal from wastewaters (Kadlec and Tilton 1979, Godfrey et al. 1985). Whereas denitrification is mainly responsible for nitrogen removal from wastewaters in wetlands, phosphorus retention is accomplished mainly by adsorption and precipitation reactions with Al, Fe, and Ca in the soil (Nichols 1983). As such, nitrogen removal does not necessarily decline with time, but the capacity of wetland soils to retain phosphorus is limited, and phosphorus retention in wetlands decreases over time (Richardson 1985).

Freshwater wetlands may also act as sinks for metals. As a result of several field and laboratory studies indicating that metals in mine drainage can be retained in Sphagnum wetlands (Huntsman et al. 1978, Wieder and Lang 1982, 1984, Kleinmann et al. 1983, Burris et al. 1984, Gerber et al. 1985, Tarleton et al. 1984, Wieder et al. 1985a), there has been an increased interest in the potential use of man-made wetland systems for the treatment of metal-enriched waters, such as those often resulting from coal and metal mining activity (Girts and Kleinmann 1986). Because metals typically do not have a gaseous phase, it is reasonable to assume that, like phosphorus, the capacity for metal retention in wetland systems is finite. However, relatively little effort has focused on developing quantitative estimates of the ultimate long-term capacity for metal retention in man-made wetland systems constructed specifically for mine drainage treatment.

[1]Paper presented at the 1988 Mine Drainage and Reclamation Conference, April 17-22, 1988, Pittsburgh, PA.

[2]Associate Professor of Biology, Villanova University, Villanova, PA, on a leave of absence as a Technical Advisor with the U.S. Office of Surface Mining, Reclamation, and Enforcement, Eastern Field Operations, Pittsburgh, PA.

Proceedings America Society of Mining and Reclamation, 1987 pp 375-381

DOI: 10.21000/JASMR88010375

Accurate estimation of the ultimate capacity for metal retention in man-made wetland systems would be useful from both practical and regulatory standpoints. From a practical point of view, it is difficult to carry out cost/benefit analyses when the ultimate capacity for metal retention in a particular wetland receiving a particular volume and chemistry of mine drainage is unknown. From a regulatory point of view, any consideration of bond release based on constructed wetland systems for mine drainage treatment cannot be objectively assessed until reliable predictions of long-term effectiveness of wetland treatment systems can be made.

In this paper, an upper limit on Fe retention in *Sphagnum* wetlands is estimated by individually considering the biological and chemical processes contributing to Fe retention in wetland ecosystems. Also, different field monitoring schemes are discussed in terms of their potential for assessing the effectiveness of metal retention within man-made wetland systems and their potential for extrapolating the long-term capacity for effective treatment of mine drainage.

UPPER LIMIT FOR Fe RETENTION

Five processes are primarily involved in Fe retention in *Sphagnum* wetlands: uptake and incorporation of Fe by growing *Sphagnum* mosses, the removal of Fe ions from solution by cation exchange, the specific adsorption of Fe onto organic matter, the formation of insoluble Fe oxides, and the formation of insoluble Fe sulfides. Based on our understanding of the biology and chemistry of each process, it is possible to estimate an upper limit for Fe retention in *Sphagnum* wetlands.

As a plant micronutrient, Fe is taken up by growing *Sphagnum*. The highest reported rate of net primary production of *Sphagnum* is 610 $g/m^2/yr$ (Wieder and Lang 1983). The highest reported Fe concentration in field-collected *Sphagnum* plant tissue is 5.8 mg/g (Rodin and Bazilevich 1967). Multiplying these two values gives an estimate of Fe uptake by growing *Sphagnum* of 3.5 $g/m^2/yr$. This estimate is generous not only because we used the highest reported values for both growth and tissue Fe concentration, but also because *Sphagnum* growth may be inhibited by the high Fe concentrations typical of AMD. For example, in a 33 da laboratory study, growth in length of *S. fallax* in solutions containing 100 mg/L Fe was reduced by 32.5% relative to control plants growing in solutions containing 0 mg/L Fe (Kearney 1986).

The binding of Fe^{2+} to negatively charged sites on the peat matrix provides another mechanism for Fe retention. We have quantified Fe retention through cation exchange by placing 5 g of dried peat into replicate flasks, and adding 100 mL of a solution containing either 0, 2, 4, 6, 8, 12, or 16 meq/L of Fe (added as $FeSO_4$; pH of each solution adjusted to 4.0). After 16 hr, the mixtures were filtered and binding of Fe^{2+} with the concomitant release of other cations from exchange sites was calculated (Fig. 1). Using the Langmuir equation, a maximum retention of Fe^{2+} via cation exchange of 204 ueq/g (5.7 mg/g) was estimated.

As with mineral soils (e.g., McLaren and Crawford 1973, Miller et al. 1983), peat can retain Fe by a chelation-like specific binding of the metal cations to sites on the organic matter matrix. Using 0.1 M $Na_4P_2O_7$ extractions (Wieder and Lang 1986), the highest organically bound Fe concentration that we have ever measured in a *Sphagnum* peat sample is 89.3 mg/g. Although little is known about the chemical nature of the binding sites on *Sphagnum* peat, it appears that the specific binding of Fe to organic matter may be a much more important mechanism for Fe retention than cation exchange in peat exposed to mine drainage.

Iron can also be retained in peat by the formation of insoluble Fe oxides. The highest concentrations of amorphous Fe oxide (oxalate extractable Fe) and crystalline Fe oxide (bicarbonate-citrate-dithionite extractable Fe; Wieder and Lang 1986) that we have ever determined in a peat sample are 62.8 and 39.0 mg/g, respectively. These peat samples were collected from Tub Run Bog, West Virginia, a naturally-occurring *Sphagnum*-dominated wetland receiving inputs of acid coal mine drainage from an adjacent abandoned coal surface mine (Wieder and Lang 1982). To what extent the formation of such Fe oxides is abiotic versus biotic is presently not known. However, indigenous populations of both Fe-oxidizing and Mn-oxidizing bacteria have been found in field-collected samples of *Sphagnum* peat (Stone 1984).

Some studies have suggested that bacterial dissimilatory sulfate reduction and the formation of Fe sulfides could play an important role in the removal of Fe from mine drainage (e.g., Tuttle et al. 1969a,b). Although sulfate reduction and the concomitant formation of Fe sulfides does occur in freshwater *Sphagnum* peat (Behr 1985, Behr 1986, Wieder and Lang 1988), there is little evidence that Fe sulfides accumulate to any significant extent in peat exposed to mine drainage (Tarleton et al. 1984, Wieder et al. 1985a, Wieder and Lang 1986). Presumably, the accumulation of Fe sulfides is precluded by their reoxidation, although at present little is known about the process of sulfide oxidation in freshwater wetland peat (Wieder and Lang 1988). Using the Cr^{2+}-reduction technique (Wieder et al. 1985b), the highest concentration of Fe sulfides (actually H_2S + S^o + FeS_2 +

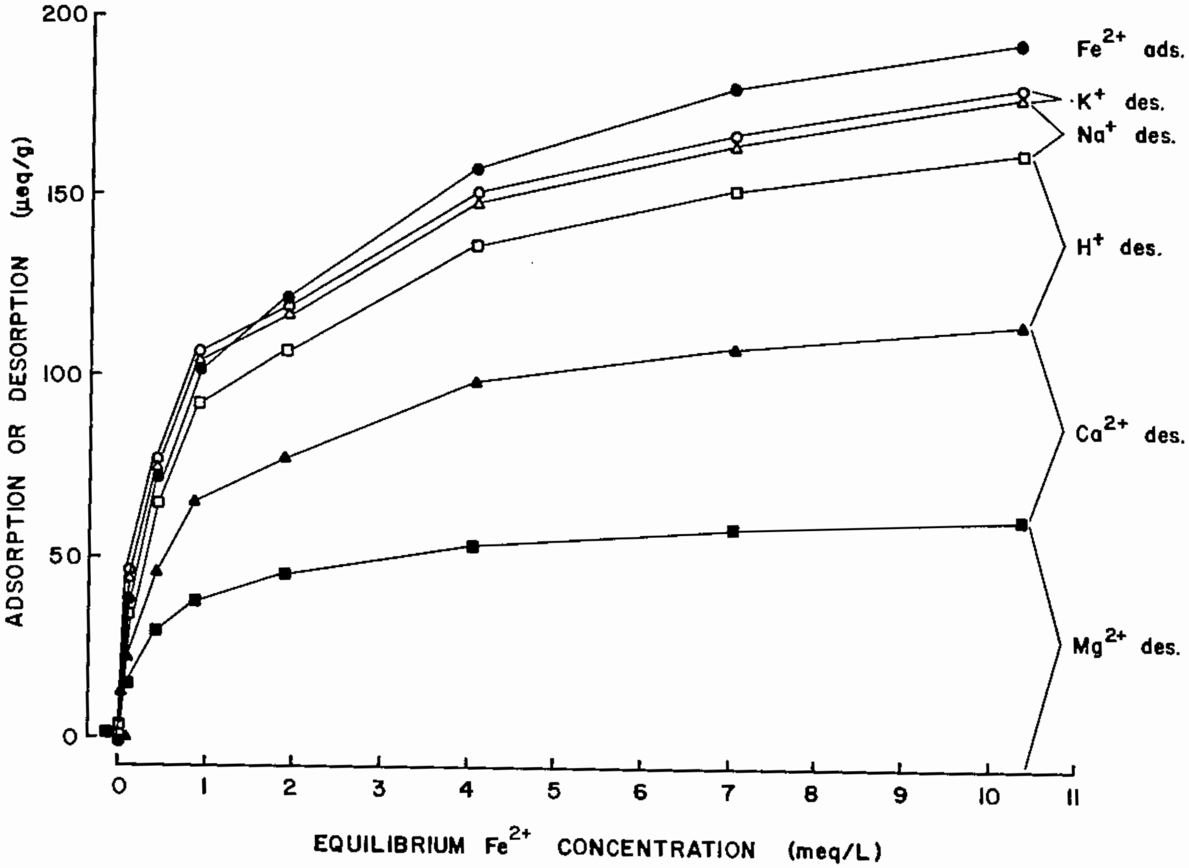

Figure 1. Adsorption of Fe^{2+} onto Sphagnum peat by cation exchange and the corresponding desorption of Mg^{2+}, Ca^{2+}, H^{+}, Na^{+}, and K^{+}.

FeS) that we have ever measured in a single peat sample is 0.7 mg/g Fe.

Assuming that it is possible to obtain maximum Fe retention by each of the above processes, an upper limit on Fe retention in a hypothetical man-made Sphagnum wetland, 40 m by 40 m, 30 cm deep was calculated (Table 1). In making these calculations, a bulk density for Sphagnum peat of 0.1 g/cm was assumed. If such a man-made wetland were exposed to mine drainage with a flow of 4 L/min and a Fe concentration of 100 mg/L (Fe loading rate of 576 g/da), it would take an estimated 44 years until Fe retention by all processes combined would become saturated.

The analysis in Table 1 reveals that incorporation of Fe by growth of Sphagnum and retention by cation exchange and sulfide formation are relatively minor contributors to overall potential Fe retention, as compared to the specific binding of Fe to organic matter and the formation of insoluble Fe oxides. It should be noted, however, that 4 L/min represents a very low flow. If the flow of mine drainage were 40 L/min (still only a moderate flow) and the Fe concentration 200 mg/L, Fe saturation of the wetland would occur in only 2.2 years. The time estimate obtained in Table 1 also assumes that it is possible to obtain the maximum Fe retention by each of the processes involved. In peat samples that have been subjected to mine drainage, either in the field or in the laboratory, rarely have we observed the maximum saturation of Fe retention by all of the processes in Table 1 (Tarleton et al. 1984, Wieder et al. 1985a, Wieder and Lang 1986). To place the estimate of the maximum potential Fe accumulation in Sphagnum peat in some perspective, an Fe concentration of 5,757 g/m^2 (Table 1) is equivalent to an Fe concentration of 19% of the dry mass!

The approach used in Table 1 has provided an estimate of the ultimate capacity for Fe retention in a man-made Sphagnum wetland exposed to mine drainage. However, data from field situations in which wetlands have been constructed specifically for mine drainage treatment are also needed. In the remainder of this paper, we discuss the relative merits and drawbacks of different monitoring schemes for assessing the effectiveness of wetland systems constructed for mine drainage treatment.

Table 1. Maximum Fe retention in a hypothetical man-made *Sphagnum* wetland.

Process	Maximum Retention (g/m)	Days to Reach Saturation
Growth of *Sphagnum*	3.5	9.7
Cation exchange	171	475
Adsorption onto organic matter	2508	6967
Formation of amorphous Fe oxides	1884	5233
Formation of crystalline Fe oxides	1170	3250
Formation of Fe sulfides	21	59
Total	5757	15994 = 44 yr

MONITORING SCHEME 1

Periodic Measurement of Inflow and Outflow Water Chemistry

The most commonly employed monitoring scheme entails the periodic measurement of inflow and outflow water chemistry. Obviously, outflow water chemistry is of particular interest, since if a wetland has been constructed for the treatment of coal mine drainage on an active mine, Federal and/or State water quality criteria must be met for water discharged from the mine site. However, outflow water chemistry alone provides little if any information about the effectiveness of the wetland for metal retention.

Often, both inflow and outflow water chemistry are determined, and a "treatment efficiency," defined as $(C_i - C_o)/C_i$, where C_i and C_o are the inflow and outflow concentrations, respectively, for a particular metal is calculated (Girts and Kleinmann 1986, Girts et al. 1987). Although this index of wetland performance is intuitively satisfying, site hydrology and frequency of sampling are two factors that must be taken into consideration when interpreting treatment efficiency data.

The observation that metal concentrations in outflow water are lower than those in inflow water is suggestive that the wetland is retaining metals, but is by no means sufficient evidence. Possible dilution of influent mine drainage by unmeasured, and perhaps not readily discernible, sources of "good quality" seepage water (i.e., with relatively low metal concentrations) could produce inflated estimates of treatment efficiency within the wetland. Thus, the index of treatment efficiency is valid only in hydrologically tight wetlands where the inflowing mine drainage represents the only significant source of water and metals and where all of the water exits the wetland either at the location of the outflow water sample or via evapotranspiration. Most man-made wetlands are situated in topographically low-lying areas, often where seeps are common. Moreover, when heavy equipment is used during construction of man-made wetlands, seepage may be enhanced as a result of soil excavation. Thus, it is likely that in many instances the condition of hydrologic tightness in a man-made wetland is not satisfied.

The calculation of treatment efficiency based on mean metal concentrations averaged over long periods of sampling may mask seasonal patterns (i.e., winter versus summer) or more short-term patterns such as those that may be associated with major rain events. For example, it is possible that a wetland may be actively retaining metals during relatively dry periods (e.g., by the formation of metal oxides during periods of low water table), but that accumulated metal oxide flocs are flushed downstream during major rain events (cf. Lang and Wieder 1985). Thus, the nature of the data base must be taken into consideration when interpreting treatment efficiencies.

Despite the potential problems in interpreting data resulting from the periodic measurement of inflow and outflow chemistry in a man-made wetland, long-term changes in treatment efficiency (i.e., a progressive decrease in treatment over several years) at a particular site may be informative, assuming that the hydrologic conditions remain relatively constant over the entire sampling period. Advantages to this monitoring scheme are the minimal effort and minimal expense required.

MONITORING SCHEME 2

Periodic Measurement of Inflow and Outflow Water Chemistry with Measurement of Inflow and Outflow Water Fluxes

The monitoring scheme described above can be improved upon substantially by the installation of instrumentation to measure influent and effluent water fluxes since both water and chemical budgets can be quantitatively estimated for a man-made wetland system. If the estimated quantity of water leaving a wetland is less than the quantity entering, and if the difference is comparable to regional estimates of evapotranspiration, then dilution of the mine drainage by good quality seepage water is probably not occurring at the site.

Once a hydrologic budget is calculated and determined to be reasonable, then periodic measurements of metal concentrations in inflow and outflow waters can be used to construct metal budgets for the wetland. The accuracy of the estimates of net retention/release of a particular metal obtained from a metal input/output budget is improved as the frequency of sampling water for chemical analysis increases. Metal budgets can be used to evaluate changes in the metal retention efficiency of a wetland either on a short-term basis (i.e. during and following a rain event), seasonally, or on an annual basis. If a trend of decreasing metal retention is obtained over time, extrapolation may provide a quantitative way of estimating the long-term capacity of a particular wetland for retaining a particular metal (cf. Richardson 1985).

Although the construction of water and metal budgets for a wetland provides a much better indicator of metal retention efficiency than the "treatment efficiency" index discussed under Scheme 1, the associated cost increase can be substantial. Continuous monitoring of water flows requires careful and costly setup, as well as a considerable time commitment involved in subsequent maintenance and data reduction.

MONITORING SCHEME 3

Periodic Measurement of Inflow and Outflow Water Chemistry with Measurement of Inflow and Outflow Water Fluxes and Periodic Analysis of the Wetland Substrate

While Scheme 2 represents a considerable improvement over Scheme 1 with respect to being able to evaluate metal removal efficiency and to project the long-term capacity of the wetland to retain metals, a potential problem with Scheme 2 is that the metal budgets are constructed using occasional measurement of metal concentrations in inflow and outflow waters. Thus, if the flushing of metals from a wetland during major rain events is indeed considerable, but rain event sampling is not carried out, the efflux of metals from the wetland will be underestimated in the metal budget calculation and wetland efficiency for metal retention will be overestimated.

Periodic determination of metal concentration in the wetland substrate can be used to verify metal accumulation determined from the metal budget calculations. Accurate estimation of metal accumulation in the substrate depends on analyzing a sufficient number of substrate samples. In addition, if the substrate samples are dried and ground prior to chemical analysis, values for water content and bulk density of the substrate must be obtained in order to estimate metal accumulation within the entire wetland. Besides providing verification for water budget calculations, trends indicating increases in metal concentrations in the substrate over time can also be used to extrapolate long-term capacity for metal retention in a wetland.

In comparison to Scheme 2, this approach to monitoring a man-made wetland involves the additional expense of collection and analysis of sediment samples.

DISCUSSION

It has been suggested that man-made wetlands may offer a low-cost approach to mine drainage treatment (Wieder and Lang 1982, Kleinmann et al. 1983, Girts and Kleinmann 1986). However, based on the analysis in Table 1, it appears that wetland treatment of mine drainage has a limited potential. Although Table 1 focuses on Fe retention in Sphagnum wetlands, it is likely that, at least qualitatively, the findings apply to other metals and to other types of wetland systems as well. The construction of wetlands may be attractive for the treatment of seeps with low flow volumes, but as the flow of the mine drainage increases and/or the metal concentrations in the mine drainage increase, the effective life-time of a man-made wetland will decrease.

In response to the increased interest in using man-made wetlands for mine drainage treatment, the U.S. Office of Surface Mining, Reclamation and Enforcement has adopted the policy that man-made wetlands may be used on active mine sites as long as a fully operational water treatment capability is in place and operational downslope from the wetland and within the permit area. A second part of that policy is that given the present state of knowledge, bonds should not be released based on the installation of man-made wetlands to treat mine drainage.

From a purely practical point of view, if the immediate goal of using a man-made wetland for mine drainage treatment is to meet Federal and/or State water quality criteria, perhaps the single most important measurement is water quality at the outflow from the wetland. Such minimal sampling, however, will provide no insight into either the efficiency of the wetland for metal retention or, and perhaps more importantly, the long-term capacity of the wetland for metal retention. Until field monitoring schemes and/or other approaches allow for the quantitative, reliable estimation of the long-term capacity for metal retention within a wetland given a particular volume and chemistry of water, the environmental and economic potentials of wetland treatment of coal mine drainage remain difficult to quantitatively assess.

ACKNOWLEDGEMENTS

Technical assistance was provided by V.A. Granus, and K.P. Heston, and E.M. O'Hara. Portions of this work were supported by grants R810082 and R812379 from the U.S. Environmental Protection Agency.

LITERATURE CITED

Behr, R.S. 1985. Sulfur dynamics in an experimentally acidified mire in northwestern Ontario. M.S. Thesis, University of Manitoba.

Brown, K. 1985. Sulphur distribution and metabolism in waterlogged peat. Soil Biol. Biochem. 17:39-45.
http://dx.doi.org/10.1016/0038-0717(85)90088-4

Burris, J.E., D.W. Gerber, and L.E. McHerron. 1984. Removal of iron and manganese from water by Sphagnum moss. pp. 1-13. In Treatment of Mine Drainage by Wetlands. J.E. Burris (Ed). Contribution No. 264, The Pennsylvania State University, University Park, PA.

Gerber, D.W., J.E. Burris, and R.W. Stone. 1984. Removal of dissolved iron and manganese ions by a Sphagnum moss system. pp. 365-372. In Wetlands and Water Management on Mined Lands. R.P. Brooks, D.E. Samuel and J.B. Hill (Eds.). Pennsylvania State University, University Park, PA.

Girts, M.A., and R.L.P. Kleinmann. 1986. Constructed wetlands for treatment of acid mine drainage: A preliminary review. pp. 165-171. In National Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY.

Girts, M.A., R.L.P. Kleinmann, and P.M. Erickson. 1987. Performance data on Typha and Sphagnum wetlands constructed to treat coal mine drainage. In Eighth Annual Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Godfrey, P.J., E.R. Kaynor, S. Pelczarski, and J. Benforado (Eds.). 1985. Ecological Considerations in Wetlands Treatment of Municipal Wastewater. Van Nostrand Reinhold Co., Inc., NY.

Greeson, P.E., J.R. Clark, and L.E. Clark (Eds.). 1978. Wetland Functions and Values: The State of Our Understanding. American Water Resources Association, Minneapolis, MN.

Huntsman, B.E., J.G. Solch, and M.D. Porter. 1978. Utilization of Sphagnum species dominated bog for coal acid mine drainage abatement. Abstracts 91st Ann. Mtg. Geol. Soc. Amer., Ottawa, Ontario, Canada.

Kadlec, R.H., and D.L. Tilton. 1979. The use of wetlands as a tertiary treatment procedure. CRC Crit. Rev. in Environ. Control 9:185-212.

Kearney, A.D. 1986. The effects of acid mine drainage on Sphagnum species: Growth, chlorophyll concentration, and plant tissue chemistry. M.S. Thesis, Department of Biology, Villanova University, Villanova, PA.

Kleinmann, R.L.P., T.O. Tiernan, J.G. Solch, and R.L. Harris. 1983. A low-cost, low-maintenance treatment system for acid mine drainage using Sphagnum moss and limestone. pp. 241-245. In Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. D.H. Graves (Ed.). University of Kentucky, Lexington, KY.

Lang, G.E., and R.K. Wieder. 1985. Modification of acid mine drainage by Sphagnum-dominated wetlands and the effect on stream water quality. pp. 176-184. In Wetlands of the Chesapeake: Protecting the Future of the Bay Environmental Law Institute and Maryland Department of Natural Resources, Easton, MD.

McLaren, R.G., and D.V. Crawford. 1973. Studies on soil copper. II. The specific adsorption of copper by soils. J. Soil Sci. 24:443-452.
http://dx.doi.org/10.1111/j.1365-2389.1973.tb02311.x

Miller, W.P., W.W. McFee, and J.M. Kelly. 1983. Mobility and retention of heavy metals in sandy soils. J. Environ. Qual. 12:579-584.
http://dx.doi.org/10.2134/jeq1983.00472425001200040030x

Nichols, D.S. 1983. Capacity of natural wetlands to remove nutrients from wastewater. J. Water. Pollut. Control Fed. 55:495-505.

Richardson, C.J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228:1424-1427.
http://dx.doi.org/10.1126/science.228.4706.1424

Rodin, L.E., and N.I. Bazilevich. 1967. Production and mineral cycling in terrestrial vegetation. Oliver and Boyd, London, England.

Stone, R.W. 1984. The presence of iron- and manganese-oxidizing bacteria in natural and simulated bogs. pp. 30-37. In Treatment of Mine Drainage by Wetlands. J.E. Burris (Ed). Contribution No. 264, The Pennsylvania State University, University Park, PA.

Tuttle, J.H., P.R. Dugan, C.B. MacMillan, and C.I. Randles. 1969a. Microbial dissimilatory sulfur cycle in acid mine water. J. Bacteriol. 97:594-602.

Tuttle, J.H., P.R. Dugan, and C.I. Randles. 1969b. Microbial sulfate reduction and its potential ability as an acid mine water pollution abatement procedure. Appl. Microbiol. 17:297-302.

Wieder, R.K., and G.E. Lang. 1982. Modification of acid mine drainage in a freshwater wetland. pp. 43-53. In Symposium on Wetlands of the Unglaciated Appalachian Region. B.R. McDonald (Ed.). West Virginia University, Morgantown, WV.

Wieder, R.K., and G.E. Lang. 1983. Net primary production of the dominant bryophytes in a Sphagnum-dominated wetland in West Virginia. The Bryologist 86:280-286.
http://dx.doi.org/10.2307/3242723

Wieder, R.K., and G.E Lang. 1986. Fe, Al, Mn, and S chemistry of Sphagnum peat in four peatlands with different metal and sulfur inputs. Water, Air, Soil Pollut. 23:381-396.

Wieder, R.K., and G.E. Lang. 1988. Cycling of inorganic and organic sulfur in peat from Big Run Bog, West Virginia. Biogeochemistry, in press.

Wieder, R.K., G.E. Lang, and A.E. Whitehouse. 1985a. Metal removal in Sphagnum-dominated wetlands: Experience with a man-made wetland system. pp. 353-364. In Wetlands and Water Management on Mined Lands. R.P. Brooks, D.E. Samuel and J.B. Hill (Eds.). Pennsylvania State University, University Park, PA.

Wieder, R.K., G.E. Lang, and V.A. Granus. 1985b. An evaluation of wet chemical methods for quantifying sulfur fractions in freshwater wetland peat. Limnol. Oceanogr. 30:1109-1115.
http://dx.doi.org/10.4319/lo.1985.30.5.1109