# METHODS FOR PASSIVE REMOVAL OF MANGANESE FROM ACID MINE DRAINAGE Arthur W. Rose<sup>1</sup>, Brent Means<sup>2</sup> and P.J. Shah<sup>3</sup>

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#### Abstract

Manganese can be passively removed from acid mine drainage if the chemical and microbial conditions are right. Consideration of Mn and Fe geochemistry indicates that Mn removal can occur at near-neutral pH in well aerated solutions from which essentially all Fe has been precipitated. Limestone forms a good substrate because of its effect on pH. Mn-oxidizing bacteria are essential for a significant rate, but a number of field tests suggest that special inoculation is not necessary, though it may improve startup and rates. Observations of field sites show that many Pyrolusite Systems and other limestone beds show problems from plugging by silt, leaves, Fe-hydroxide, Al-hydroxide and other materials. Observations at one limestone bed indicate that Mn precipitation is more rapid near the water surface, probably because of dissolved  $O_2$  depletion below the surface. Several examples of open limestone channels show good Mn removal, and such channels may be a satisfactory alternative to beds. A Mn removal rate of 2 to  $10 \text{ g/m}^2/\text{d}$  may be obtainable, but further study is needed to clarify the kinetic relations.

### Introduction

Passive removal of acidity, iron and aluminum from acid mine drainage has been extensively discussed in recent years, but much less attention has been focused on manganese. Although the consequences of elevated Mn are less severe than the other metals, and questioned by many, current laws require Mn levels in mine discharges to average less than 2 mg/L. Several technologies for passive Mn removal have been described, but little information is available on their success or implementation. The intent of this paper is to describe these methods and to present some information on their success and problems. A related presentation on these methods is by Rose et al. (2003).

# **Chemistry of Manganese Removal**

Chemically, Mn is somewhat similar to Fe. In the reduced  $Mn^{2+}$  state, Mn is relatively soluble as  $MnSO_4^{\circ}$  (aq.) at least up to pH 8 (Figure 1). At higher pH, it can precipitate as  $MnCO_3$ (rhodochrosite) and (at low  $CO_2$ ) as  $Mn(OH)_2$ . In contrast, under oxidizing conditions, Mn in the 3+ and 4+ oxidation state is relatively insoluble in the form of  $MnO_2$ ,  $Mn_2O_3$ ,  $Mn_3O_4$  and related compounds. This behavior is illustrated on Figure 1, an Eh-pH diagram for Mn as compared to Fe. Based on this diagram, it is evident that removal of Mn from AMD requires either high pH or strong oxidation combined with near-neutral pH.



**Figure 1.** Eh-pH diagram for Mn, calculated from data in Geochemist's Workbench. Shaded area shows insoluble phases under the indicated conditions. Clear area shows soluble Mn. Birnessite =  $MnO_2$ ; todorokite approximated as  $Mn^{II}Mn^{IV}{}_{3}O_7$ ; bixbyite =  $Mn_2O_3$ ; rhodochrosite =  $MnCO_3$ ; alabandite = MnS. Diagram also shows limit of Fe(OH)<sub>3</sub> (am) solubility. Fe(OH)<sub>3</sub> precipitates at A. Mn oxide can precipitate at B.

The diagram, drawn for concentrations of  $SO_4$  and carbonate species typical of many AMD waters, shows that under relatively reduced conditions where Fe is in solution as  $Fe^{2+}$  (point A), Mn is very soluble as the ion pair  $MnSO_4^{\circ}$ . However, near the upper limit of the diagram where oxygen is abundant (point B), Mn is insoluble as birnessite ( $MnO_2$ ) and todorokite, a complex oxide of variable composition containing  $Mn^{3+}$  and  $Mn^{4+}$  and usually Ca, Na or other cations. At pH below about 7, these solid phases can precipitate only from highly oxygenated solutions, but at higher pH the high oxygen content is less crucial. The diagram clearly shows that if appreciable  $Fe^{2+}$  is present in solution, Mn cannot precipitate at near-neutral pH. For Mn to precipitate, the water must be well oxygenated to the extent that essentially all Fe is insoluble, and pH should be near neutral or above.

The second problem of Mn removal is that Figure 1 shows <u>equilibrium</u> conditions, but oxidation from  $Mn^{2+}$  to  $Mn^{3+}$  and  $Mn^{4+}$  by dissolved O<sub>2</sub> is kinetically slow. For example, Diem and Stumm (1984) found that aerated  $Mn(NO_3)_2$  solutions stored at pH 8.4 for 4 to 7 years showed negligible precipitation. By pH 9 to 9.5, oxidation rate increases dramatically, so that

half the dissolved Mn is oxidized in times of minutes to hours, even under abiotic conditions (Hem, 1964).

Many factors affect the rate of oxidation, including pH,  $O_2$  content, light, surfaces of Mnand Fe-oxides, bacteria, and other cations and anions in solution. Under abiotic conditions at a given pH, the rate of Mn oxidation and precipitation has been found to increase with concentration of dissolved Mn and with the abundance of Mn-oxide and hydroxide surface, according to the relation

 $d[Mn]/dt = -k_o[Mn] - k_1[Mn][MnO_2]$  (1) where [Mn] is the concentration of dissolved Mn<sup>2+</sup> species, [MnO<sub>2</sub>] is the surface area of Mn oxide precipitate, t is time, and  $k_o$  and  $k_1$  are rate constants. In other words, the higher the concentration of dissolved Mn, the faster the rate of oxidation and Mn removal from solution, and the greater the amount of Mn-oxide or hydroxide precipitate present, the faster the Mn removal. The Mn oxidation is autocatalytic, because precipitation of some Mn accelerates oxidation of additional Mn.

In addition to catalysis of Mn oxidation by Mn oxide surfaces, many other surfaces are also effective. Sung and Morgan (1981) found that an Fe-oxide (lepidocrocite) surface increased oxidation rates, but amorphous silica delayed oxidation. Junta et al. (1992) showed that oxidation of Mn at the hematite surface was more rapid than on albite surfaces.

Manganese can be oxidized by a number of genera of bacteria, fungi and yeasts, including Leptothrix, Metallogenium, Arthrobacter, Pedomicrobium, Pseudomonas, and others (Ghiorse, 1984; Brock et al., 1994, Ghiorse and Ehrlich, 1992). These bacteria are aerobic heterotrophs which use dissolved oxygen to oxidize organic matter as a source of energy. In the common cases, the Mn is oxidized and precipitated in the filamentous sheath surrounding a group of cells. It is not clear whether the Mn oxidation is used to obtain energy or is incidental to other cellular processes. Fungi can be very important Mn-oxidizers, and some Mn-oxidizing bacteria use a copper-containing enzyme in the oxidation process (Souren, 2001).

At near-neutral pH values, the term  $k_o[Mn]$  in eq. (1) is very small, as indicated by the experiments of Diem and Stumm (1984) cited above. If Mn oxidizing bacteria are present, the rate of Mn oxidation may be approximately proportional to the abundance of bacteria and to dissolved Mn<sup>2+</sup> concentration, so that

 $d[Mn]/dt = -k_1[Mn][MnO_2] - k_2[Mn][bact]$ (2) where [bact] is the abundance of bacteria. If this relation holds for an Mn<sup>2+</sup> solution flowing through a bed with constant abundance of Mn-oxide and bacteria, the concentration of Mn vs. distance in the bed is expected to have the negative exponential (first order) form shown in Figure 2. Initially, removal of Mn is rapid at high Mn concentration and decreases as Mn concentration decreases. The Mn concentration decreases exponentially toward zero with flow down the bed. In a real case, the abundance of Mn-oxide and bacteria may decrease along the bed so that Mn removal requires longer retention time.



**Figure 2.** Models for kinetics of Mn removal, applied to data from the PBS site. A constant rate of 12.3  $g/m^2/d$  brings Mn to 0 at about 23 m from the inflow point. A first order rate (negative exponential) gradually approaches zero. Both models are calibrated by the observed Mn at 18 m.

The rates of Mn oxidation and reduction are also affected by sunlight, which is known to accelerate both Mn oxidation and Mn oxide reduction and dissolution. Scott et al. (2002) showed that in a fast-flowing mountain stream, the net photocatalytic effect enhanced Mn oxidation and precipitation, but they recognized some reverse effects. The enhancement effects may be due to increased production of  $O_2$  by algae, and to pH effects. Marble et al. (1999) showed that Mn removal in Pinal Creek, AZ was biotic, but they could not detect an effect of Mn oxide surface.

Adsorption or coprecipitation of Mn by Fe oxides and other colloidal occurs to a minor extent at moderate pH to high pH. Calculations using PHREEQC (Parkhurst, 1995) indicate that for Mn/Fe = 0.25, the % adsorbed is <1% at pH 5, and is only about 20% at pH 10. At lower Mn/Fe ratios, the effect could be more significant. Most Fe-oxides are precipitated at acid pH, when Mn is not adsorbed.

#### **Manganese Removal in Limestone Beds**

A number of workers have reported experiments and treatment systems in which Mnbearing solution flows through limestone beds. Experiments comparing a limestone bed with a gravel bed (aluminosilicate rock) showed that the limestone bed was much more effective in removing manganese (Sikora et al., 2000). Manganese at levels of 8 to 20 mg/L was removed to concentrations less than 1 mg/L in less than 10 m. The higher pH in the limestone system is probably at least part of the reason for the higher removal rate.

The most common method using a limestone bed is the patented "Pyrolusite Process" of Vail and Riley (1995, 1996, 2000). In this method, a bed of 2 to 8 cm limestone fragments is inoculated with Mn-oxidizing bacteria cultured on the water to be treated. Several different Mn-oxidizing species may be inoculated to different parts of the bed to accommodate differing Mn

concentrations,  $O_2$  levels, etc. (Robert Riley, personal communication). A small wetland usually precedes the limestone bed to generate dissolved organic matter for microbial metabolism. The bed should be lined so that it does not dry out at low flow, and to minimize competition from soil bacteria. A retention time of 1.25 to 3 days is recommended (Allegheny Mineral Abatement, no date). The bed should contain baffles to force the flow into the deeper part of the bed and then back to the surface. The limestone bed should be built up above the ground surface so that the water level is below the surface and water does not pond on the surface, capturing leaves.

Data on 10 Pyrolusite and related systems has been collected (Table 1, 2). The originators of the Pyrolusite System suggest that some sites were not constructed properly and the name should not be used. In particular, the Swisstock #2 and Stroud systems were not specifically designed by Allegheny Mineral Abatement, though they were inoculated. Swisstock #1 encountered much higher flows (up to 340 L/min) than the design flow of 60 L/min. Middle Branch was built without baffles and had too high an outlet level. However, for the purposes of this paper, the term is used for any site inoculated by Allegheny Mineral Abatement, which includes all sites in Table 1 except one at Middle Branch.

At most of the systems, Mn is effectively removed, to levels less than 1 mg/L. Iron and aluminum are also removed. However, problems and shortcomings of the method are noted at some sites.

The most common problem is that the influent area of the limestone bed becomes plugged by silt, leaves, algae, organic matter, Fe-oxyhydroxides, Al hydroxides, or other material. At the Swisstock #1 system, the bed worked very well for about two years, but then became plugged with leaves and organic matter, in part because of high flows. The result was that water flowed over the top of the bed, even at low flow, and was only partly treated (Figure 3). No monitoring or maintenance was done on this system, which failed shortly after bond release. The Swisstock #2 site also plugged and became ineffective. At the Squatter Falls (Glenwhite) system, the influent contained considerable Fe (average 28 mg/L). The Fe and Mn were removed by the bed, but Fe precipitate plugged the inlet area within a few weeks so that reworking of this area has been required frequently. Similar but much less severe problems from Fe and Al precipitates have been observed at Laurel Run and PBS, requiring occasional reworking of the inlet area. At Middle Branch, both systems developed extensive cover by dirt washed in with the influent water during high flow, and the beds flooded to the surface. The dirt formed the substrate for grass and algae, and the limestone exhibited a white coating that may be Al hydroxide and/or CaCO<sub>3</sub>. The cover and coatings prevented contact with limestone and led to flow over the surface and only partial Mn removal (Figure 4). The outflow point has since been lowered and the influent sediment cut off, and the beds are now functioning better.



**Figure 3**. Manganese concentration in the inflow and outflow of the Swisstock #1 Pyrolusite System.



Figure 4. Manganese concentration in the inflow and in the outflow of the inoculated and non-inoculated limestone beds at Middle Branch.

These observations indicate that careful design and construction is essential, and that some monitoring and maintenance must be done to identify and remedy problems.

Limestone fragments in the beds are typically coated with Mn oxides, but observations and calculations indicate that plugging with Mn oxides is not an immediate problem. For typical Mn concentrations and flow rates, the pore space will accommodate many tens of years or more of Mn precipitate. Black coating from the PBS site was scraped off and analyzed by X-ray diffraction. It is dominantly todorokite (approximately (Ca,Na)Mn<sub>6</sub>O<sub>12</sub>), an Mn oxide with a tunnel structure containing the additional cations. This mineral is recognized to form in marine manganese nodules and apparently is favored by the elevated cation concentration in AMD.

Another possible problem is that the deeper parts of the bed are apparently not very effective in removing Mn. A pit dug in the limestone bed at PBS encountered a zone of fragments cemented with Mn oxide and other minerals approximately at the water level in the bed. Fragments in this zone were 80 to 90% covered with Mn oxide coatings with thicknesses of 0.2 to 0.5 mm. At 0.3 m deeper, fragments were only about 50% coated with thicknesses of about 0.2 mm, and the fragments were loose and easily dug. This vertical change correlates with a decrease in dissolved oxygen from about 40 to 50% of saturation near the water surface, to less than 10% at depth. As indicated in Figure 1, oxidation and precipitation of Mn oxides is promoted by high oxidation levels. At depth, O<sub>2</sub> has been consumed, probably by oxidation of organic matter and Mn, and oxidation conditions are not optimum for Mn removal. The specialized bacteria added by AMA may partly counteract low O<sub>2</sub>, but low O<sub>2</sub> cannot be optimum.

The patents and description of the Pyrolusite System imply that cultivation of special bacteria is desirable for Mn removal. A test of this hypothesis was conducted at the Middle Branch site. Two beds were constructed with identical specifications, and the flow of influent water was split to provide identical water chemistry to the beds. One bed was inoculated by Allegheny Mineral Abatement and the other was not. Although both beds suffered from plugging, as discussed above, the non-inoculated bed performed similarly to the inoculated bed. It is possible that Mn oxidizing bacteria have been transferred to the non-inoculated bed on the feet of birds or animals, but if this is so, then transfer and inoculation by the requisite bacteria is relatively easy. Observations at other sites, discussed below, indicate that Mn-oxidizing bacteria are widely distributed, and if conditions are favorable, Mn-oxidizing bacteria will naturally populate the bed.

Robbins et al. (1999) and Brant and Ziemkiewicz (1997) described a limestone bed at Shade Mining in Somerset Co., PA which successfully treats influent with 12 to 25 mg/L Mn to discharge effluent with <2 mg/L Mn. The limestone fragments became coated with a black slime. In this coating, manganese precipitates were noted on bacteria, cyanobacteria, diatoms and green algae. This bed was not inoculated with special bacteria. Lab experiments showed that limestone fragments coated with black Mn oxide and containing microbes performed much better than fresh limestone, and that aeration slightly improved the removal rate.

## **Other Types of Field Treatment Systems and Experiments**

Appreciable removal of Mn along flowing channels has been observed at a number of sites. On a field trip with the 1996 meeting of the American Society for Surface Mining and Reclamation in Tennessee, two Mn-removal channels were observed. At the Sequatchie Valley Coal Co. near Dunlap TN, AMD with about 25 mg/L Mn was pumped from a reclaimed surface mine and treated by ponds and wetlands to remove Fe to levels <1 mg/L. The effluent (pH 7.6) passed along a 0.5-mile channel to a pond before discharge to a stream. Along this channel and in the pond, black Mn precipitate was precipitating naturally on the sides and bottom. Flow in the channel was rapid, so the water was well aerated. At the second site, the Skyline Coal Co. Glady Fork project, a serpentine channel lined with limestone was removing small amounts of Mn from a flow of treated water.

A third Mn-removing channel is at a surface coal mine in north-central PA. Effluent draining an area surface mined and reclaimed a couple of years earlier flowed from the caved portal of an older small underground mine. Limestone had been added to the surface mine spoil, so that the flow from the caved adit had pH 6.55, alkalinity 347 mg/L, Fe <0.1 mg/L and Mn 2.16 mg/L, temperature 9C and a flow rate of 95 L/min. The water flowed down a channel about 0.6 m wide for 23 m, with numerous small riffles. At this location, the Mn had decreased to 0.76 mg/L. The channel contained filamentous algal growths, and was in open sun a few hours per day. Attached to the algae and to the channel bottom were numerous black Mn-rich nodules up to 5 mm diameter, and some algae were colored black with possible Mn precipitate.

At a mine in Australia, a system of ponds and channels was used to remove elevated Zn, Mn and Fe from 5000  $m^3/d$  of processing effluent (Jones et al., 1995). The Fe and part of the Zn and Mn were removed along a steep channel followed by a settling pond. After this treatment, remaining Mn at levels of 2 mg/L was removed to <0.1 mg/L in 1000 m of algae-filled channel at pH 8. The algae were coated with black Mn precipitate. Removal of Mn was higher during daytime than at night.

At the Long Valley site in Bradford Co., PA, AMD flows at 270 L/min down a steep channel for 23 m. The Mn concentration is 10 mg/L at the inflow to the channel, 0.5 mg/L at the outflow in winter, and non-detected in summer (Jon Dietz, personal communication, 2002).

These cases indicate that Mn removal can be effective from well aerated, Fe-free water flowing along channels. Presence of limestone and algae appears to be favorable. Removal rates are not well established, but probably are at least 2 g/m<sup>2</sup>/d, and may be as high as 10 g/m<sup>2</sup>/d (but see later discussion of removal rates).

Several experiments have been conducted on removal in ponds and tanks. Thornton (1995) tested Mn removal from effluent of an ash disposal pond using two limestone-filled tanks. The concentration of Mn decreased from 3.5 mg/L in influent to 0.5 mg/L in effluent. Phillips et al. (1994) compared three ponds for removal of 8 mg/L Mn. A pond with a limestone substrate and seeded with a floating cyanobacterial mat was more effective than ponds lacking the mat. Clayton et al. (1999) tested a combination of algal pond scum and a limestone bed in aerobic wetland experiments and found very effective Mn removal.

Partial Mn removal is reported in some SAPS-type vertical flow systems. At the McKinley VFS near Clarion, PA, Terry Morrow reports partial removal of Mn. Lab experiments at the Cook Run area, PA show removal of Mn from 50 mg/L to 11 mg/L along with Fe and Al in bench tests of a compost limestone reactor (J. Schueck, personal communication). A possible removal mechanism in these cases is co-precipitation with Fe oxides at pH values above 7.

#### **Rates of Manganese Removal**

Several approaches can be used to express rates of removal and to design treatment units. The correct method depends on the parameters determining the rate and the way that they interact. Unfortunately, we do not have enough data to determine the correct formulation.

Vail and Riley (2000) suggest a retention time of about 3 days as a design criterion. However, the decreased effectiveness of the deeper part of the bed at PBS suggests that retention time in a deep bed may be of decreased effectiveness because of dissolved  $O_2$  depletion. Also, a simple retention time does not take account of high concentrations of influent Mn, which probably require longer retention.

If dissolved  $O_2$  is the rate-limiting reactant and is supplied from the water surface, then a constant areal removal rate (i.e.,  $g/m^2/d$ ) may be appropriate. This approach implies that (3)

$$d[Mn]/dt = k$$

In integrated form, for this relation,

 $[Mn] = [Mn_o] - kt$ 

(4)

where  $[Mn_o]$  is influent Mn concentration. This relation is shown graphically on Figure 2. Several qualifications must be noted. First, dissolved O<sub>2</sub> is probably high at the inflow point, so that reaction is faster there. Second, once Mn concentration becomes low, in the downflow parts of the bed, dissolved  $O_2$  may no longer be a limiting factor. Finally, this relation obviously does not apply when [Mn] = 0.

Estimated rates in  $g/m^2/d$  are given in Table 2. One qualification is that for most systems, we have only the influent and effluent concentrations, but in actuality, Mn removal may be essentially completed in the first part of the bed, with little change in the remainder of the flow path. This seems to be the case at PBS, based on our data (i.e., Mn is 0.33 mg/L at both 30 m and at the outflow at 64 m). The areal removal rates are minimum values, because of this effect. The higher rates may express the real rate. The measurement for PBS at 18 m indicates a rate of 12 g/m<sup>2</sup>/d, which is similar to the rate at Swisstock #1. Thus, a rate of 10 g/m<sup>2</sup>/d or better may be achievable in Pyrolusite and similar systems.

Equations 1 and 2 suggest that the removal rates are not constant, but are higher for higher concentrations of Mn. If rate is proportional to [Mn], the Mn concentration along the bed is expected to be a negative exponential (Figure 2), or is linear on a plot of log  $(C/C_o)$  vs. time (or distance). Calculations and log-linear plots have been made assuming a first order rate expressed by equations of the form

d[Mn]/dt = -K[Mn]S	(5)
$Log([Mn]/[Mn_0]) = -2.3 \text{ KSt}$	(6)

where t is the retention time (hr), S is the "concentration" of surface area of fragments  $(m^2/m^3)$  or bacterial-coated surface and K is a removal rate(hr<sup>-1</sup>m<sup>-2</sup>).

For PBS, the data for the point at 18 m from the inflow gives a rate of about  $10^{-4} \text{ hr}^{-1}\text{m}^{-2}$  for K (log K = -4.06). Log rates for other sites are similar or lower, possibly because most Mn removal occurs in only the first section of bed. Therefore, a tentative first-order removal rate of about  $10^{-4} \text{ hr}^{-1}\text{m}^{-2}$  may be estimated. Using this approach, the bed size and retention time will vary with the influent Mn concentration and the desired effluent value. However, more data is needed to verify this method.

Clearly, we need to establish the applicable rate law in order to design these systems reliably. We are currently planning field measurements for this purpose.

#### Conclusions

The many experiments and treatment systems discussed here demonstrate that Mn removal is possible from near-neutral solutions. For satisfactory performance, essentially all dissolved Fe and Al must be removed (<1 mg/L), and the water should be well aerated. Limestone is a desirable substrate because of its effect on pH. Bacteria are probably always involved as catalysts, but inoculation with specialized bacteria is not essential, though it may hasten startup and generate somewhat higher removal rates. Careful design and construction are essential, as is continuing monitoring and maintenance to correct any problems that may develop.

Measurements indicate that dissolved  $O_2$  is depleted at depth in the current design of Pyrolusite Systems. Therefore, deep beds are probably not optimum in effectiveness. Evidence in some experiments indicates that exposure to sunlight with resulting growth of  $O_2$ -generating algae and cyanobacteria is beneficial, at least during warmer weather. For these reasons, open limestone-lined channels of appropriate retention time may be preferable to deep beds.

The appropriate rate law operative in Mn removal in beds and channels is not clear. If the rate is constant (zero order), then rates in  $g/m^2/d$  are appropriate. Values in the range 2 to 10  $g/m^2/d$  are obtained at field sites. If instead the rate law is first order (proportional to Mn concentration), then a value of  $10^{-4}$  hr<sup>-1</sup>m<sup>2</sup> is estimated as described in the text. This rate law implies that rates in  $g/m^2/d$  and retention times will vary depending on influent Mn concentration, flow rate and active surface area of the bed. Probably the truth is that the form of the rate law differs under differing conditions.

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# Table 1. Characteristics of Pyrolusite and Related Systems

Site	Location	Length	Width	Depth	Ls.Mass	Ls. Size	Built
		m	m	m	Т	cm	
K & J	Cambria Co., PA	27	2.9	0.9		2.5	10/91
Swisstock 1	Cambria Co., PA	61	2.9	0.9		2.5	4/94
Swisstock 2	Cambria Co., PA	29	1.5			2.5-5	3/95
PBS	Somerset Co., PA	64	4.6	0.9		1.2	1/98
Laurel Run	Westmoreland Co., PA	46	12.3	1.5	1911	2.5-6	6/97
Stroud	Cambria Co., PA	61	4.6			5-7.5	2/98
Sq.Falls (Glenwhite)	Blair Co., PA	65	25	2.13	5400	1-6	5/99
Cambria G	Cambria Co., PA	80	18.5			6	3/00
Middle Br.	Clinton Co., PA	31	17	1.52	1140	6	8/01
Middle Br.	Clinton Co., PA	31	17	1.52	1140	6	8/01

# Table 2. Data on Pyrolusite and related systems Data for Mn, Fe, Al in mg/L

Site	I	Mn		Fe		AI		эΗ	Flow	$N^1$	Period	Rate
	in	out	in	out	in	out	in	out	L/min			g/m²/d
K&J	27.8	0.4	0.08	0.03			4.4	7.5	5.7 (E <sup>2</sup> )	67,85	10/91-4/98	2.9
Swisstock 1	16.4	4.4(1.6 <sup>3</sup> )	0.2	0.2	6	2	3.9	6.4	110 (E)	61	4/94-8/98	13.2
Swisstock 2	8.5	5.6	0.4	0.2	7.8	2.9	3.6	5.6	76 (E)	33	3/95-6/98	7.3
PBS	28.1	1.1	0.01	0	4.7	0	5.0	7	25	42	1/98-11/02	3.2
Laurel Run	11.6	0.1	4.8	0.03	7.8	0.1	3.5	7.3	60	31	10/97-3/02	1.8
Stroud	8(14 <sup>4</sup> )	1.2	3.9	0.7	1.9	<0.5	5.6	6.6	46(E)	4,43	3/98-10/01	3
Glenwhite	5.7	0.4	28	0.3	0.8	0.2	3.3	7.2	255	33	5/99-2/02	1.2
Cambria G	129	41	2	<1	<1	<1	6.3	6.7	19 (E)	1	6/01	1.6?
Middle Br. I	20	6.7	4.1	3.6	14.9	5.8	5.2	6.6	140?	11	8/01-7/02	5.1?
Middle Br. II	20	6	4.1	0.7	14.9	2.7	5.2	6.6	140?	9	10/01-7/02	5.3?

<sup>1</sup> Number of samples (inflow, outflow)
 <sup>2</sup> E = estimate flows, others based on weirs
 <sup>3</sup> First 19 months

<sup>4</sup> Including 3 preconstruction samples