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Technical Article

A Comparison of Filtered vs. Unfiltered Metal Concentrations in Treatment Wetlands

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Abstract. Filtered vs. unfiltered metals analyses are compared from two demonstration wetlands built by ARCO in Butte, Montana. The Wetlands Demonstration Project 1 (WDP1) facility was an anaerobic, subsurface flow wetland, whereas the Colorado Tailings (CT) facility was a lime-added, aerobic system. At both sites, a significant fraction of each metal of concern (Cu, Cd, Zn, Fe, and Mn) existed in particulate form in some parts of the treatment system. The anaerobic WDP1 wetland removed dissolved metals to very low levels, but had mixed success in filtering out fine-grained sulfide precipitates of Cu, Cd and Zn. The CT wetland showed better capacity to remove particulate metals. Based on these two case studies, the importance of obtaining both filtered and unfiltered (total recoverable) samples at treatment wetlands is stressed.

Key words: Wetland; Metals; Butte, Montana

Introduction

This paper addresses the relationship between metal concentrations in filtered (0.45 µm) vs. unfiltered samples at two demonstration wetland facilities in Butte, Montana. Although both facilities treated similar waters, they differed greatly in form and function (Pantano et al. 1999). Wetlands Demonstration Project One (WDP1) relied on anaerobic, subsurface-flow conditions to precipitate heavy metals as insoluble sulfides. In contrast, the Colorado Tailings (CT) demonstration wetland relied on lime treatment, enhanced by biological influences, in an aerobic environment. Both facilities were funded and built by the Atlantic Richfield Company (ARCO) in the Spring of 1996, and operated through December of 1998. During this time, the chemistry of influent, effluent, and internal waters were monitored closely by Montana Tech staff and students.

The question of whether to collect filtered vs. unfiltered water samples for monitoring purposes is an important one. Most regulatory standards apply to unfiltered, "total recoverable", or "total metal" samples. For this reason, monitoring efforts at mine sites or treatment facilities always include unfiltered samples, whereas comparatively few (or no) filtered samples may be taken. However, in geochemical modeling, it is much more useful to have dissolved (i.e., filtered) metal concentrations to calculate mineral saturation indices or aqueous speciation. For example, Frandsen and Gammons (1999) have recently modeled the fate and transport of dissolved metals in the sulfidic treatment waters of WDP1. Finally, a comparison of filtered vs. unfiltered concentrations can provide insight into hydrogeochemical processes: for example, whether metal exceedances are due mainly due to chemical vs. physical problems.

Based on a review of the literature and personal communication with other investigators in the field of wetlands remediation, it is evident that monitoring of treatment wetlands at hard rock mine sites has historically focused on unfiltered (total) metal analyses. Although the importance of distinguishing particulate vs. dissolved metal concentrations in these systems is recognized, few published studies have directly addressed this question. The databases for the WDP1 and CT demonstration wetlands in Butte are somewhat unusual, in that paired filtered and unfiltered analyses were collected for every sample during the 3-year monitoring period.

Site Descriptions

Over a century of mining, milling, and smelting activities in the Butte area have severely degraded the quality of local groundwater and surface water. Water treated at WDP1 came from Butte's Metro Storm Drain (MSD), which is a man-made ditch collecting storm water and contaminated groundwater discharging along the base of Butte Hill. The CT facility treated groundwater collected by a hydraulic control channel in a broad area of historic wetlands along Silver Bow Creek (the headwaters of the Clark Fork River). The inlet water at both facilities had similar chemical characteristics. Table 1 lists some of the important water quality parameters. Although pH was near neutral, the waters contained elevated sulfate and highly elevated zinc, manganese, copper, and cadmium.

WDP1 wetland

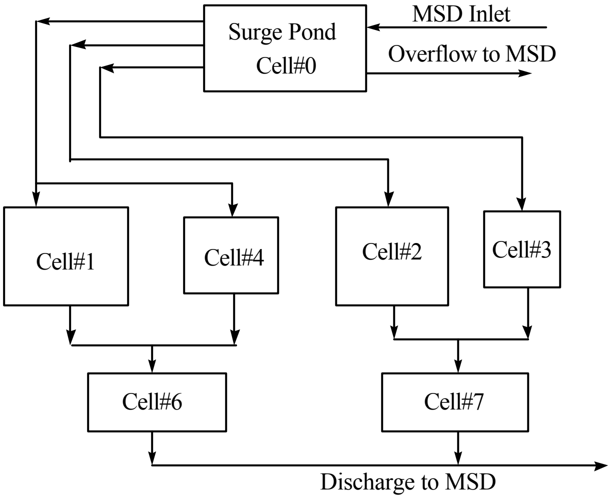

Figure 1. Schematic diagram showing flow of water in the WDP1 Wetlands

The WDP1 facility (Figure 1, Table 2) consisted of a free water "surge pond" (Cell 0), four subsurface-flow anaerobic cells (Cells 1 to 4), and two aerobic polishing cells (Cells 6 and 7). MSD water was pumped into the surge pond, which settled out suspended particles and provided hydraulic head for the rest of the facility. Water exiting the surge pond passed through one of the four anaerobic cells. These cells were filled with ~ 1/2 inch river gravel and limestone fragments, and were planted at the surface with cattails. Compost was added to the

Table 1. Selected parameters for filtered influent and effluent waters

	WDP1-influent[1]	WDP1-Effluent[1]	CT-influent[2]	CT-effluent[2]	WQB-7[3]
PH	6.80	6.84	6.7	9.4	-
SO_4^{2-}, mg/kg	472	289	399	367	-
Fe, µg/kg	28.8	18.0	1350	14.7	300 *
Zn, µg/kg	9330	10.5	11,600	104	110 **
Mn, µg/kg	6680	3640	6830	41.9	50 *
Cu, µg/kg	123	3.6	768	19.4	12 **
Cd, µg/kg	40.5	0.51	39.6	1.2	1.1**
As, µg/kg	8.6	11.9	25.5	11.9	18 *

[1] Filtered influent and effluent for Cell 2, measured on 8/17/98.

[2] Filtered influent and effluent for CT wetland, measured 9/28/98.

[3] Montana WQB-7 standards for: *human health; ** aquatic life chronic exposure @100 mg/kg $CaCO_3$ alkalinity.

Table 2. Description of wetland cells at WDP1

Cell	Description	Specifications	Residence time
0	settling pond	area = 7,000 ft^2, volume = 40,000 ft^3	10 days @ 20 gpm
1	anaerobic wetland	horizontal subsurface flow volume = 30,000 ft^3, depth = 2.5 ft	9.4 days @ 5 gpm
2	anaerobic wetland	horizontal subsurface flow volume = 20,000 ft^3, depth = 4 ft	6.2 days @ 5 gpm
3	anaerobic wetland	upwards subsurface flow volume = 12,000 ft^3, depth = 6 ft	3.7 days @ 5 gpm
4	anaerobic wetland	horizontal subsurface flow volume = 15,000 ft^3, depth = 2.5 ft	4.8 days @ 5 gpm
6	aerobic wetland	shallow ponds and riffles area ~ 2,000 ft^2	~ 2 days @ 10 gpm
7	aerobic wetland	as for Cell 6, area ~ 6,500 ft^2	~ 6 days @ 10 gpm

substrate of Cells 2 and 3 as an additional source of organic carbon for heterotrophic bacteria. It was hoped that conditions in the anaerobic cells would be conducive to bacterial sulfate reduction (BSR), and subsequent precipitation of zinc, copper and cadmium as insoluble sulfide minerals. Subsequent monitoring revealed this to be the case for most of the operating period, although BSR rates were greatly reduced in the winter months, especially for Cell 4 (Gammons et al. 2000). Water exiting the anaerobic cells flowed to one of 2 aerobic polishing cells (Cells 6 and 7), which consisted of a series of shallow pools and riffles. The purpose of these cells was to re-aerate the water, oxidize any excess H_2S, and hopefully remove residual iron and manganese as oxy-hydroxide phases. The entire facility treated between 15 and 30 gpm of MSD water during the 3 years of operation. Further details on the operation and performance of WDP1 are given in Mueller et al. (1997), P. Zhang (1997); J. Zhang (1997), Jones (1997), Wang (1998), Zhang (1998), Mainzhausen (1998), Gammons et al. (1998), Frandsen and Gammons (1999), Frandsen (2000), and Gammons et al. (2000).

CT wetland

The CT facility (Table 3, Figure 2) consisted of 3 free water ponds (FW01, FW02, FW03) set in sequence, separated by 2 permeable treatment walls (TW01, TW02). Groundwater collected from the hydraulic control channel was sent through a liming circuit, and then flowed into FW01. From FW01, water passed by gravity through TW01 to FW02, and similarly through TW02 to FW03. An optional recirculation line allowed water exiting FW03 to be pumped back

Table 3. Description of wetland cells at Colorado Tailings

Cell	Description	Specifications	Residence time[1]
FW01	free water pond	130' long x 185' wide x 0-4.5' deep	2.8 days
TW01	treatment wall	horizontal subsurface flow 185' wide x 20' (top); 40' (base)	~ 0.4 days
FW02	free water pond	130' long x 185' wide x 4.5' deep	5.6 days
TW02	treatment wall	horizontal subsurface flow 185' wide x 20' (top); 40' (base)	~ 0.4 days
FW03	free water pond	130' long x 185' wide x 4.5' deep	5.6 days

[1] Residence times calculated for 100 gpm through-flow, assuming no losses to groundwater

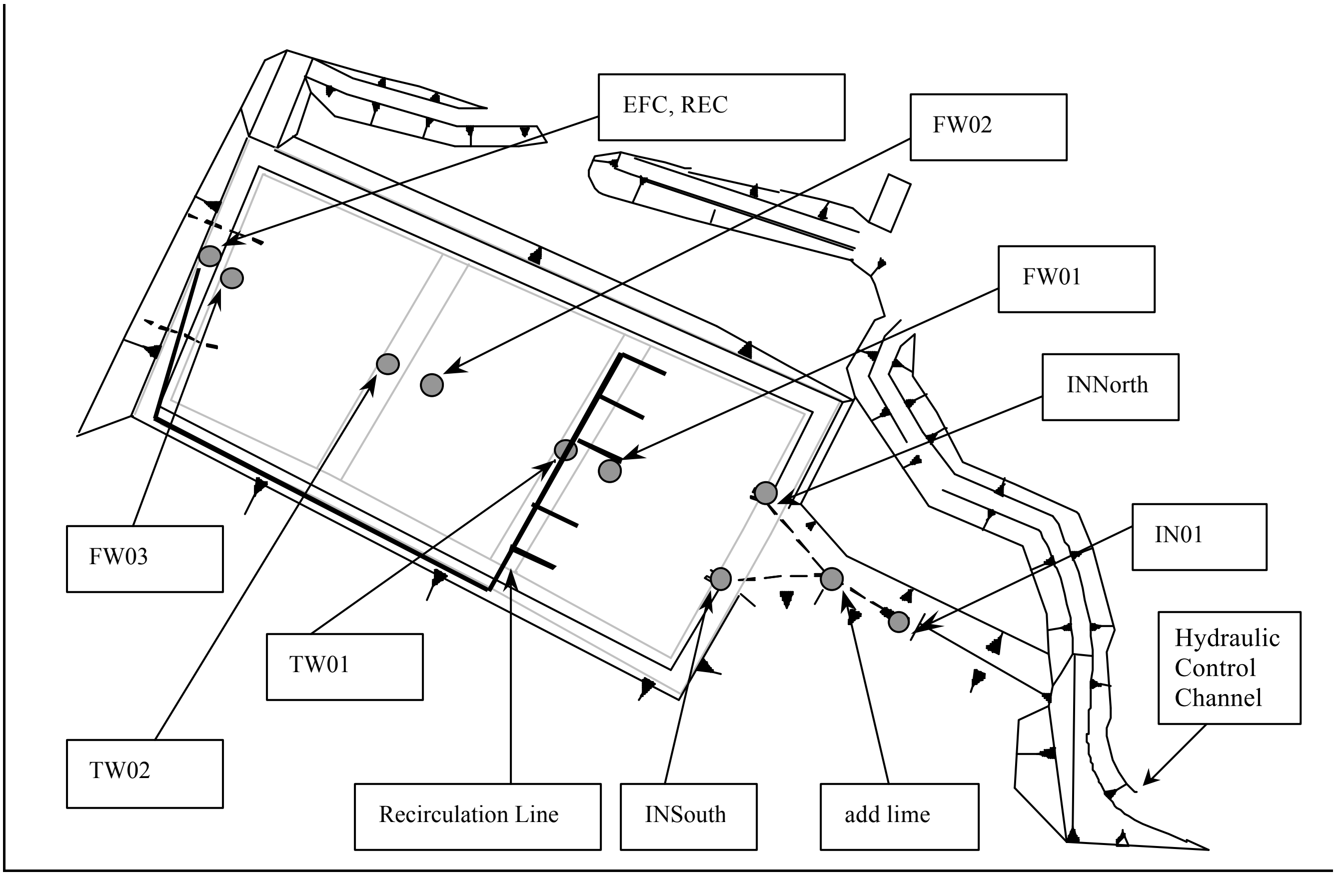

Figure 2. Schematic diagram of Colorado Tailings demonstration wetlands (after Mulholland 1999)

into FW01. Most metal attenuation in the CT wetlands occurred in FW01, presumably by precipitation of carbonate or oxy-hydroxide minerals following adjustment of pH to the optimal range of ~ 9 to 9.5. Additional alkalinity and pH increase were provided through photosynthesis, especially during the summer months. The treatment walls consisted of porous river gravel, although a small amount of compost was added to TW02. The purpose of the treatment walls was to act as hydraulic barriers, and to assist in filtration of suspended particles. The addition of compost to TW02 was to test whether bacterial sulfate reduction would occur. Subsequent monitoring showed no signs of BSR activity, presumably due to the short residence time of water in TW02. Between 1996 and 1998, the CT wetland treated an average of ~ 100 gpm of contaminated water. Further details on the operation and performance of the CT wetland can be found in Lyons (1998), Sharp (1999), Mulholland (1999), and Pantano et al. (1999).

Methods

At WDP1, inlet and outlet waters were sampled monthly for each wetland cell. Outlet samples for the anaerobic cells were collected from a tightly sealed, cylindrical sump, located immediately downstream of each cell's buried outlet distribution pipe. The samples were collected using a special device consisting of two articulated bamboo poles, one of which was secured to a 60 mL HDPE bottle, and the other to the bottle's cap. The tip of the device was lowered to the depth at which the sample was to be taken, and then the bottle lid was slowly screwed on by rotating the movable pole. Sampling in this way avoided the need of a pump, which otherwise may have caused turbulence and re-suspension of solid particles.

Filtered samples were collected using disposable plastic syringes and 0.45 µm CAMEO 25GA acetate-plus membrane filters, each equipped with a 1 µm glass prefilter. Filtered and unfiltered samples were acidified in the field to 2% HCl or HNO_3, using Fisher Trace Metal Grade or Baker Instra-Analyzed acids. The samples were analyzed for the elements As, Al, Ca, Cd, Cr, Co, Cu, Fe, S, P, Pb, Ni, K, Mg, Mn, Na, Si, and Zn, using a Perkin Elmer Optima 3000 DV ICP-AES Spectrometer. Analytical protocol for this instrument followed SW-846 Method 6010B, Inorganic Analysis by ICP-AES and EPA 600 Method 200.7, Inorganic Analysis by Inductively Coupled Plasma Analysis.

"Dissolved" vs. "filtered" vs. "particulate" vs. "colloidal" metals

To be truly dissolved, a molecule will typically have a diameter of < 100 Angstroms, or 0.01 µm (Stumm and Morgan 1996). Solids with diameter between 0.01 and ~ 1 to 10 µm are usually termed colloids, whereas coarser solids are usually referred to as suspended particles. If present, some colloidal solids could have passed through the 0.45 µm filter membranes used in this study. In this case, the filtered analysis would yield an over-estimate of the true dissolved metal concentration. Although the term "filtered" is more precise, the term "dissolved" is also used in this paper to refer to metals that passed through a 0.45 µm filter. The term "particle" is used in this paper to describe any solid that was removed by a 0.45 µm filter.

The effect of filter pore diameter on particle retention was investigated early on in the WDP1 project. Successive filtrations of duplicate samples were performed using 0.45 and 0.10 µm membrane filters (P. Zhang 1997). The results showed significantly lower "dissolved" concentrations using the 0.10 µm filters for certain metals, including copper. This simple experiment emphasizes the difficulty of obtaining aqueous samples in which all of the metals of interest are truly in the dissolved state.

Results

The following discussion will focus on the metals zinc, copper, iron, and manganese, although cadmium and sulfur are also briefly discussed. Many other contaminants were monitored at the WDP1 and CT demonstration projects, but are not shown here for lack of space. Most of the major trends are well represented by the chosen suite. Results for each element are summarized on plots of filtered vs. unfiltered metal concentration. Superimposed on the diagrams are lines corresponding to unfiltered:filtered ratios of 1:1, 10:1, 100:1, etc.. If all of the contaminants in a given sample were present in the dissolved state, the analyses plot along the 1:1 line. If particulate metal was present, the data plot below the 1:1 line. The 10:1 and 100:1 lines are shown for reference, and correspond to 90% and 99%, respectively, of total metal in particulate form.

WDP1 wetland

Figure 3 contains plots of filtered vs. unfiltered metal concentration at 4 sampling stations: 0E = water exiting the surge pond; 2E = effluent from anaerobic Cell 2; 4E = effluent from anaerobic Cell 4; and 6E = effluent from aerobic polishing Cell 6. It is interesting to compare results for Cells 2 and 4. Cell 2 had an optimal design, with a longer residence time, and compost blended into the substrate. In contrast, Cell 4 had no compost in the substrate and a shorter residence time. Residence times varied during the course of the project, depending on the volume of water passing through the cells (usually between 5 and 10 gpm). Also, thick frost zones in winter decreased the effective volume of the substrates, decreasing the residence time proportionately (Gammons et al. 2000). Tracer studies (Jones 1997; Mainzhausen 1998) showed that flow through each of the subsurface anaerobic cells was somewhat heterogeneous, with zones of relatively faster or slower groundwater movement.

The anaerobic cells at WDP1 were initially constructed with a porous filter fabric near both the inlet and outlet distribution pipes. After ~ 1 year of operation, the filter fabrics became clogged, and were removed. The inlet fabrics were coated with a brownish layer of clay, ferric oxy-hydroxide, and organic material washed in from the surge pond. The outlet fabrics had a thin black coating of a mixture of organic material and fine-grained metal sulfides. The fact that metal sulfides accumulated at the outlet fabric emphasizes the fact that the substrates were ineffective at completely removing the sulfide particles.

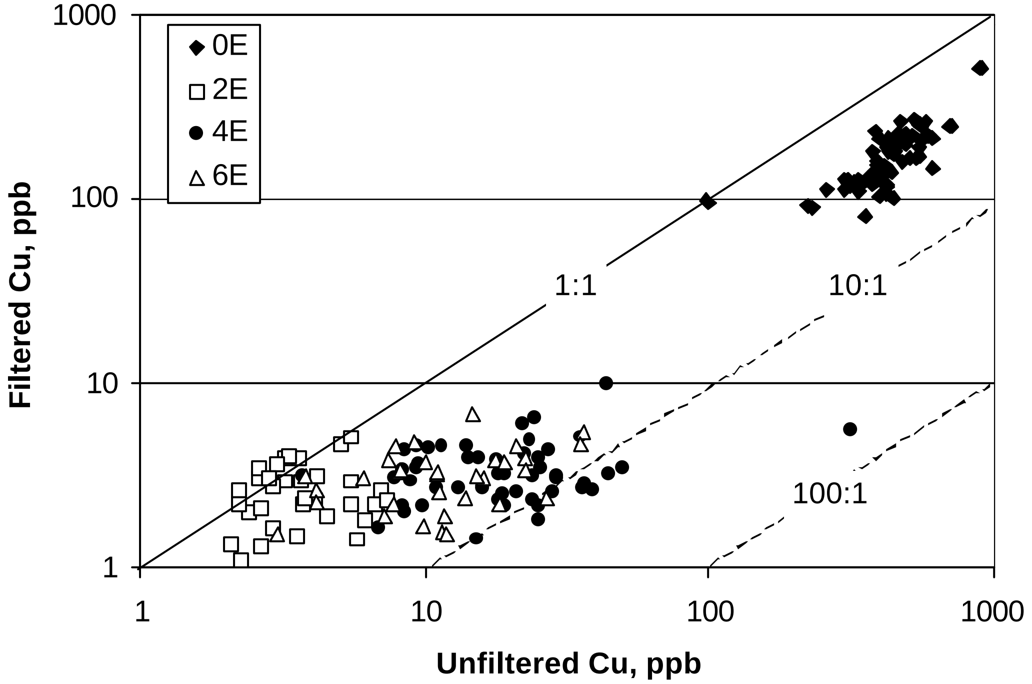

Figure 3a. Filtered vs. unfiltered Cu at WDP1 wetlands

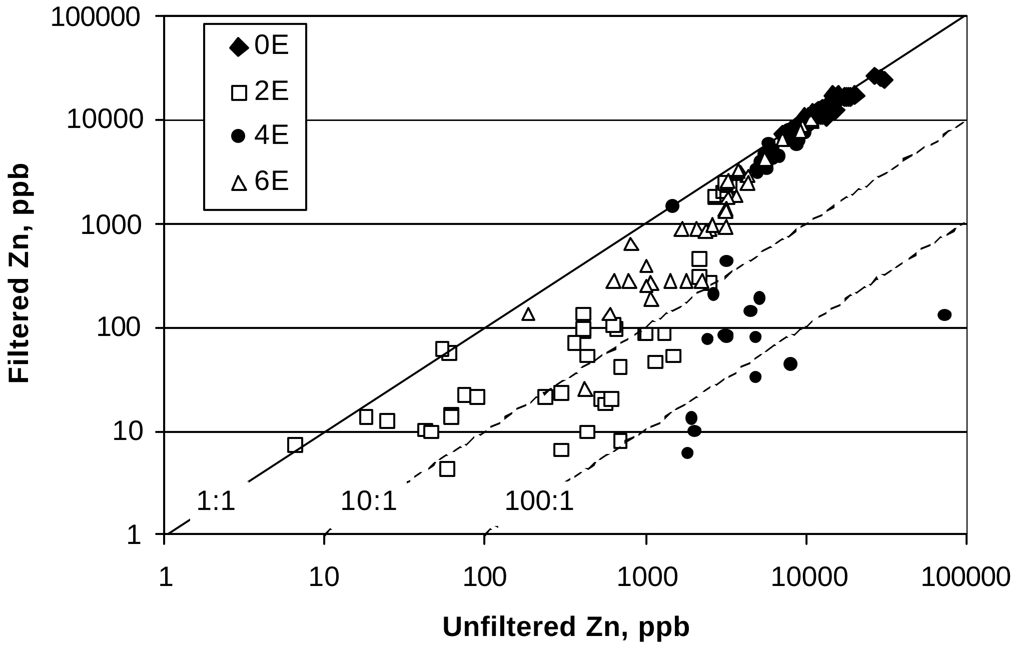

Figure 3b. Filtered vs. unfiltered Zn at WDP1 wetlands

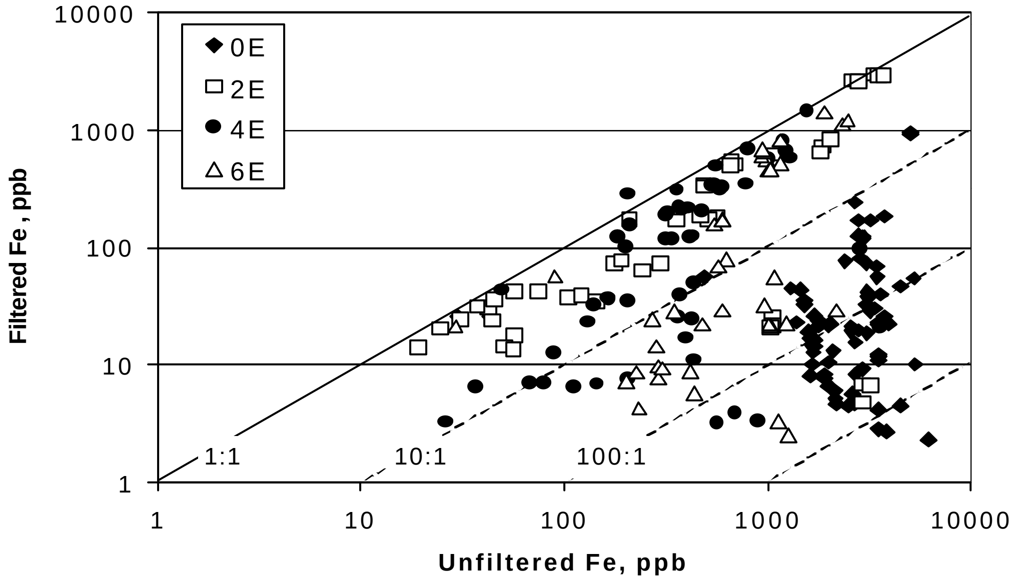

Figure 3c. Filtered vs. unfiltered Fe at WDP1 wetlands

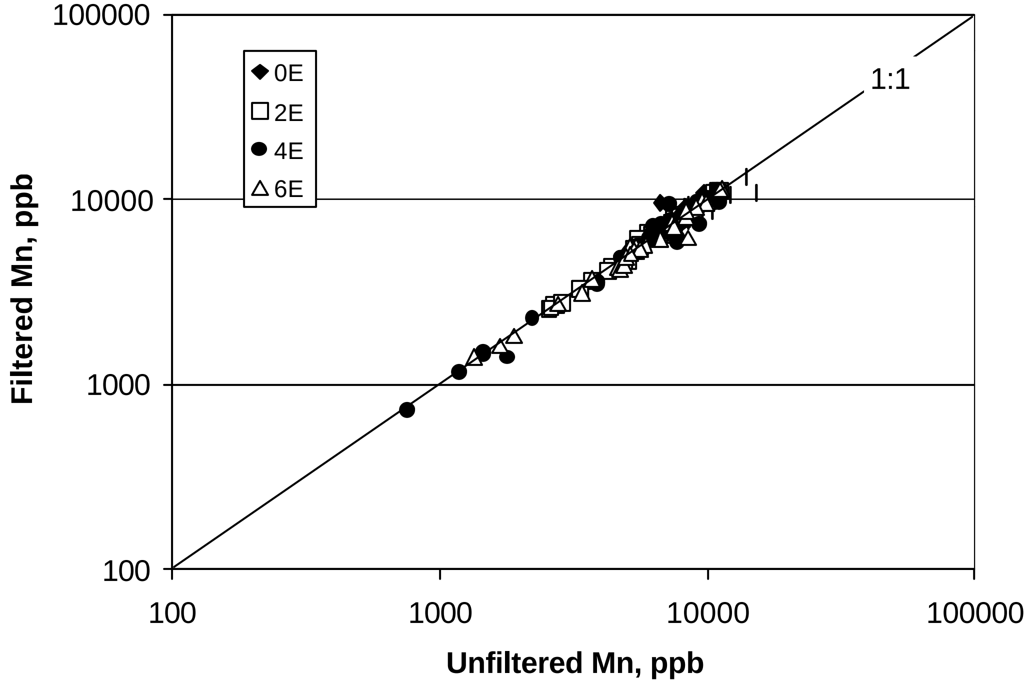

Figure 3d. Filtered vs. unfiltered Mn at WDP1 wetlands

Results for *copper* (Fig. 3a) show that this metal entered the anaerobic cells in both dissolved and particulate form. The identity of the particulate fraction is not known, but could have included detrital grains of Cu-bearing minerals washed from upstream mine waste, or, more likely, Cu adsorbed onto ferric-hydroxide, clay, or organic surfaces. Both anaerobic cells removed filtered Cu to very low levels (<10 ppb for most samples), presumably by precipitation of Cu-sulfides (Zhang 1998; Wang 1998). However the Cell 4 effluent consistently had elevated copper in particulate form. In fact, the majority of unfiltered Cell 4 samples exceeded aquatic standards for Cu (12 ppb at 100 ppm $CaCO_3$ alkalinity), whereas filtered analyses were mostly <10 ppb. This problem was much less evident for Cell 2. Besides the fact that Cell 2 had a longer residence time, the "redox front" for the onset of BSR occurred much closer to the outlet distribution pipe in Cell 4 vs. Cell 2. As a result, Cu-sulfide particles formed in Cell 4 had little opportunity to be filtered out before exiting the cell.

Zinc (Fig. 3b) left the surge pond in dissolved form, but showed much the same trends as for copper once in the anaerobic cells. Overall, zinc was much more difficult to remove consistently than copper at WDP1, especially in the winter. Poorer removal efficiency during the colder months has been attributed to a combination of decreased residence time (from freezing of the upper layers of substrate), and lower rates of bacterial sulfate reduction (Gammons et al. 2000). Decreased residence time could also account for poorer filtration of sulfide particles in the winter months. Figure 3b shows that > 90% of zinc leaving Cells 2 and 4 was present as particles for many sampling dates. Unfiltered zinc concentrations in Cell 4 effluent often exceeded 1 mg/kg, whereas filtered zinc concentrations for the same samples usually met chronic aquatic life standards (110 ppb at 100 ppm $CaCO_3$ alkalinity). Imaging of secondary precipitates from Cell 2 by scanning electron microscopy showed abundant, framboidal clusters of small ZnS spheres, with diameters in the range 0.1 to 10 µm (Frandsen 2000). Clearly, a significant fraction of these fine-grained precipitates were able to pass through the porous gravel substrates. Figure 3 suggests that many of these particles re-dissolved in the aerobic polishing ponds (Cell 6), releasing Zn back into aqueous solution.

Although not shown, *cadmium* showed very similar trends as for copper and zinc in the WDP1 treatment cells. Dissolved cadmium was consistently removed to values near the instrumental detection limit (<1 ppb), whereas particulate cadmium often exceeded 10 ppb, especially for Cell 4 effluent.

Results for *iron* (Figure 3c) show that >90% of this element entered the anaerobic cells in particulate form. The shift towards the 1:1 line in the anaerobic cells indicates loss of these particles, probably due to a combination of reductive dissolution of ferric oxy-hydroxide particles, as well as filtration by the gravel substrates. Iron tends to be lower in Cell 2 effluent than Cell 4, presumably due to the higher H_2S levels in Cell 2 (usually >1 mg/L), which decreased the mobility of dissolved iron by precipitation of iron sulfide phases. SEM-EDX analysis of Cell 2 substrates showed the presence of FeS_x solid particles, both as framboids and as grain coatings (Frandsen 2000). Also, most of the ZnS precipitates were found to contain a significant amount of iron (~11 atomic % FeS component, average of 10 semiquantitative analyses), as well as minor amounts of manganese (~3% MnS component). It is interesting to note that natural sphalerites from mineral deposits often contain elevated iron, especially in reducing environments (Barton and Skinner 1979).

In general, particulate iron levels in the aerobic polishing pond (Cell 6) were similar or slightly higher than those for the Cell 2 and Cell 4 effluent waters. This indicates re-oxidation of dissolved Fe^{2+} exiting the anaerobic cells to form a second generation of ferric oxy-hydroxide compounds. These secondary precipitates could potentially be helpful in attenuating any residual metals exiting the anaerobic cells (e.g., arsenic), via adsorption or co-precipitation. However, no clear evidence for this mechanism was found at WDP1.

The plot of filtered vs. unfiltered *manganese* concentration (Fig. 3d) shows no evidence of particulate manganese in any of the WDP1 cells. In general, Mn attenuation at WDP1 was poor. Thermodynamically, manganese should have been removed as oxy-hydroxide precipitates in the oxygenated waters of the surge pond or the aerobic polishing cells. However, despite residence times of up to 10 days in Cell 0, this reaction did not occur. In fact, the only Mn attenuation observed at WDP1 occurred in the anaerobic cells, and only in the summer months. Removal of dissolved manganese in this case was tentatively attributed to co-precipitation with calcite in micro-environments of enhanced bacterial sulfate reduction and alkalinity production (Gammons et al. 2000). More recent SEM work has shown that Mn occurs as a minor but significant impurity in ZnS particles, possibly as a MnS-ZnS solid solution (Frandsen 2000). Partial attenuation of manganese in the summer months as a $CaCO_3$-$MnCO_3$ or MnS-ZnS solid solution is consistent with the fact that the solubilities of $CaCO_3$, $MnCO_3$ and MnS all decrease with increase in temperature. Also, increases in alkalinity and H_2S in the anaerobic cells were greatest during the summer months (Frandsen 2000; Gammons et al. 2000).

Also present in the aerobic polishing cells were abundant colloidal *sulfur* particles. These particles formed via incomplete oxidation of excess H_2S (leaving the anaerobic cells) to elemental S, via the reaction:

$$H_2S(aq) + 1/2O_2\ (g) \rightarrow S(s) + H_2O \qquad (1)$$

This reaction was catalyzed by bacteria, as evidenced by the accumulation of a mix of white and purple biofilms near the influent pipes to Cells 6 and 7. During the warmer months, the S particles were sufficiently abundant to give the water in the polishing ponds an overall appearance of dilute skim milk. It is not known whether these extremely fine-grained S particles could play an important role as sorbates for residual metals exiting the anaerobic cells. What is certain is that elemental sulfur particles, besides being an eyesore, are a minor source of acidity, as the particles will eventually oxidize to sulfate, releasing protons in the process:

$$S(s) + 3/2O_2\ (g) + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad (2)$$

The rate of oxidation of elemental S particles was not determined in this study, but is likely to be complexly linked to microbial activity (Ehrlich 1996).

CT wetland

Plots of filtered vs. unfiltered metal concentrations are shown in Figure 4 for three sampling stations: FW01, FW02, and the effluent to FW03. Data from the treatment walls are not shown for clarity.

Results for *copper* are shown in Figure 4a. As for WDP1, copper entered the CT wetlands in a mix of dissolved and particulate forms. Over 90% of the dissolved copper was removed in FW01 after lime addition, presumably by precipitation of Cu-carbonate or oxy-hydroxide phases. Some copper particles remained suspended in FW01, but either settled by gravity or were filtered out by the time the waters made it to FW02.

Zinc entered the CT wetlands in dissolved form (Fig. 4b), but roughly 99% of this dissolved metal was removed in FW01 following lime treatment. Again, the precise form of this attenuated zinc is not known, but was most likely carbonate or oxy-hydroxide phases. Figure 4b shows that these solids were slow to settle out in FW01 (~2.8 day residence time), but were effectively removed by the time water got to FW02.

Results for *iron* are shown in Figure 4c. As for WDP1, iron entered the CT wetland in particulate form. Most of these particles settled out in FW01, but a small % remained suspended all the way to the effluent sampling station. Dissolved iron concentrations decreased by roughly an order of magnitude in FW01, and remained low for the remainder of the facility.

The filtered vs. unfiltered diagram for *manganese* (Fig. 4d) shows several interesting trends. As for WDP1, manganese entered the CT wetland in dissolved form. Following addition of lime, dissolved Mn was lowered by almost an order of magnitude. No suspended particles formed during this process, however. A very similar trend was observed for calcium (not shown). There is no question that calcium removal occurred by precipitation of calcite. Therefore, it is reasonable to suppose that Mn was also removed by precipitation of $MnCO_3$ (rhodocrosite), $CaMn(CO_3)_2$ (kutnahorite), or a Ca-Mn carbonate solid solution. In FW02 and FW03, dissolved Mn was further decreased, and particles containing Mn became evident. The delayed oxidation of Mn^{2+} and subsequent precipitation of Mn oxy-hydroxide minerals best explain these observations (Mulholland 1999). It is possible that Mn^{2+} oxidation was catalyzed by passage of water through the gravel treatment walls. For example, published studies have shown that Mn^{2+} oxidation rates increase in the presence of certain metal oxy-hydroxides (Davies and Morgan 1989). Biological processes may also have played a role, as FW02 and FW03 were productive in terms of algal growth and photosynthesis.

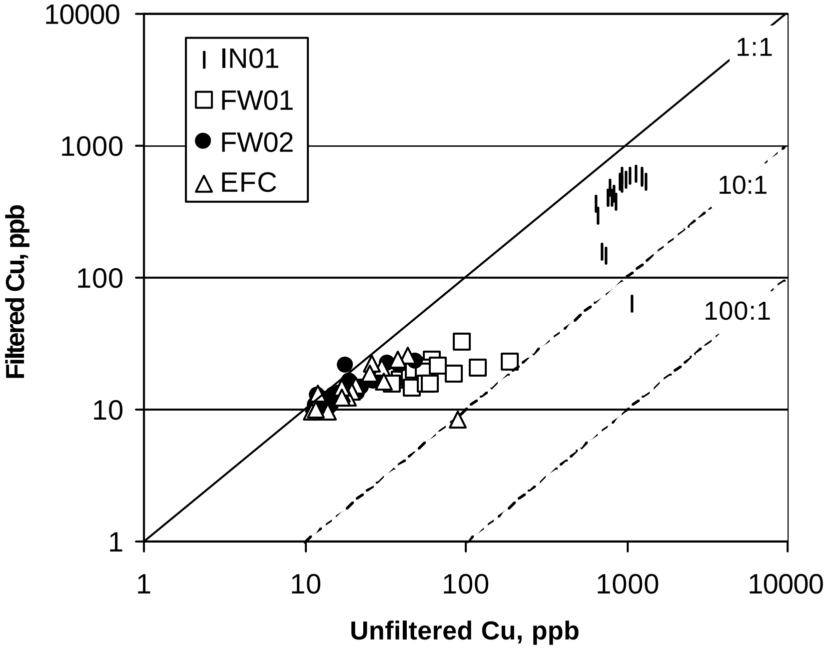

Figure 4a. Filtered vs. unfiltered Cu at CT wetland

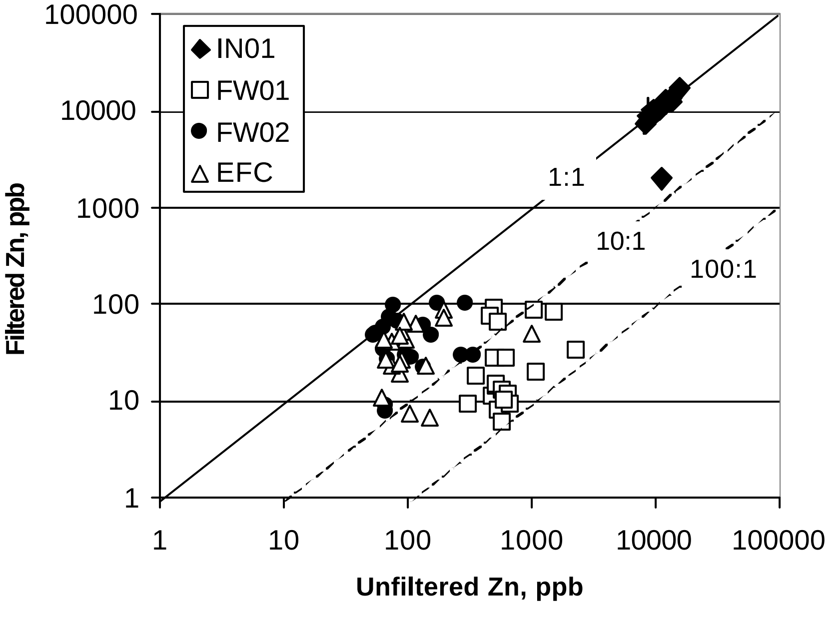

Figure 4b. Filtered vs. unfiltered Zn at CT wetland

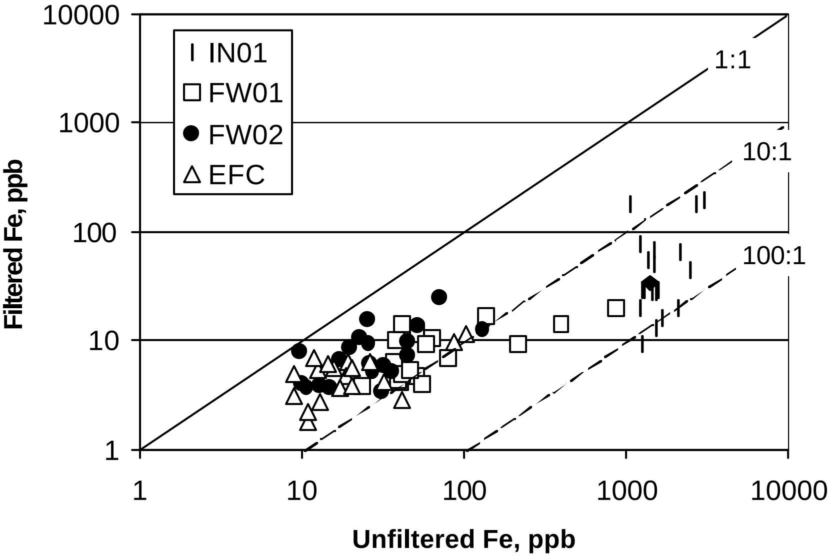

Figure 4c. Filtered vs. unfiltered Fe at CT wetland

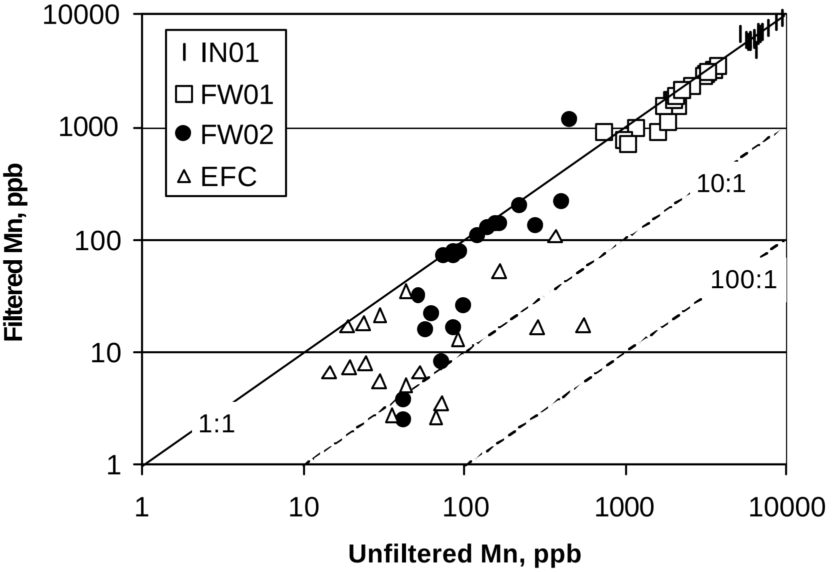

Figure 4d. Filtered vs. unfiltered Mn at CT wetland

Discussion

A detailed discussion of the performance of the WDP1 and CT wetlands is beyond the scope of this paper. However, a few significant observations can be made regarding the question of particulate vs. dissolved metals. In the case of WDP1, all of the dissolved metals of concern except manganese were effectively removed, provided residence times were >4 days (Gammons et al. 2000). However, particulate metals were a significant concern, especially for zinc, copper and cadmium. Production of H_2S by bacterial sulfate reduction resulted in very rapid precipitation of metals as fine-grained framboidal sulfide particles. Some of these particles passed through the anaerobic cells, and were not filtered by the porous gravel substrates. Re-oxidation of these sulfide particles in downstream waters could release some or all of this metal back into soluble form.

The inability of the subsurface-flow wetlands to filter out suspended particles was not foreseen at the beginning of the WDP1 project, although a similar problem has been noted in other anaerobic wetlands treating metals pollution (J. Gusek personal comm.). Increasing the residence time of the wetland may alleviate this problem. However, at WDP1, we found that ZnS particle retention did not correlate well with residence time (Gammons et al. 2000). Furthermore, the thickness of the winter ice zone in the subsurface treatment cells increased away from the inlet distribution pipes (Mainzhausen 1998; Gammons et al. 2000). The implication is that, without insulation, larger subsurface wetlands could have thermal problems in a particularly cold winter. Decreasing the particle size of the substrate might also increase the efficiency of filtration, but would likely reduce the hydraulic conductivity of the cell, thereby shortening the lifespan of the facility.

Although the CT wetland removed dissolved metal concentration of Cu, Cd, and Zn to somewhat higher levels than in WDP1, the CT facility was more dependable in terms of suspended particle removal. Thus, fewer instances of an exceedance with respect to total metals were noted at CT. However, the existence of particles in the first free water pond at CT emphasizes the need to consider this aspect of the problem in designing the overall size and residence time of a full-scale wetland. In addition, any event that could serve to shorten residence time and/or create turbulence (e.g., storm surge, heavy winds, scouring of sediments by melting and shifting ice), could potentially re-suspend metal particles, possibly leading to undesirable releases, especially in the absence of any hydraulic barriers.

This paper has documented the usefulness of collecting filtered as well as total recoverable samples from treatment wetlands. Diagrams of filtered vs. unfiltered metal concentration, such as those in this paper, help to explain problems related to treatment efficiency, and also yield clues regarding the physical and chemical processes that control the fate of metals in the system. Any equilibrium modeling of aqueous metal transport and deposition (e.g., Frandsen and Gammons 1999) requires dissolved metal concentrations as input. Use of total metal analyses will give misleading results if a significant portion of the metal was present in particulate form. While collecting dual samples for every monitoring point of interest may be uneconomical, we recommend that at least some filtered samples be included in the monitoring program (e.g., 10% of the total matrix), and that these results be reported.

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