Wood Cadillac Mine Tailings: Designing a Biofilter for Arsenic Control

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Abstract

The Wood Cadillac mine site, in Northwestern Quebec, features sulphide-poor, but As-rich, tailings, laid down between 1939 and 1949. Restoration first focussed on the mechanical stabilization of tailings. A reducing biofilter was planned for the passive treatment of As-contaminated seep and surface waters. The As load, in these conditions, is precipitated as As_2S_3 (orpiment). The efficiency and performance of the wood wastes intended to be used in the biofilter first needed to be determined. Various types of barks were tested in water-saturated columns at different flow rates. Sulphate reduction and As precipitation did occur with a removal often higher than 80 %. The precipitated solid was stable under acid leach down to pH 2. Barks with a component from deciduous trees best performed, more than coniferous barks. Thirty years old wastes were still reactive, but to a much lesser degree. As expected, performance increased with residence time. The data allowed for the design and implementation of a 50 m X 57 m, one meter thick, biofilter with a vertical flow and a residence time of 25 hours.

Introduction

The Wood Cadillac Mine Site is located 6 km East of Cadillac, in Northwestern Québec. It features tailings produced by gold mining of Archean rocks at the Wood Cadillac and Central Cadillac Mines between 1939 and 1949. The bulk of the tailings (350 000 t) is spread over 21 ha in an unconfined wedge shape deposit, with a maximum thickness of 3 m. An additional ~100 000 t is dispersed over 3 km along a small brook, the Pandora Creek. Site characterization started in 1995, and remediation followed with the physical stabilization of the tailings, first at the mine site, then along the Pandora Creek (Tassé, 1996, 1997; Dessau-Soprin, 2001). Meanwhile, the problem of chemical contamination was addressed in the lab.

The Wood Cadillac tailings are sulphidic (1.08 % S as sulphide), with a slight excess of buffering capacity over acid producing capacity (36.6 *vs* 33.7 kg $CaCO_3$/t; Tassé, 1996). Arsenic is the main concern, since that element exhibits a good mobility in the environment. The tailings contain on the average 3 600 ppm As, located in arsenopyrite and arsenous pyrite (average of 0.4 w. % in the later; S. Fortin, personal communication). Concentrations vary from 60 to 1 200 ppb in the pore water of the water-saturated tailings, with an average of 325 ppm. Pandora Creek's water contains from 100 (high waters) to 220 (low waters) ppb As.

Taking into considerations the size of the site, the amount of trough flow by runoff and groundwater, the success of an other reducing device operated in a nearby location (East Sullivan Mine Site, Val d'Or; Germain et al., 2000), the implementation of a reducing biofilter rapidly shows up as a technique that could control efficiently and in an economic way the amounts of arsenic leaving the site. In such a filter, metal and sulphate bearing waters are driven into an organic-rich milieu that allows sulphate reduction and metal precipitation as MeS, here As as As_2S_3 (orpiment). However, some laboratory data were needed in order to define how the biofilter would perform and to scale it up.

Experimental set up

At normal surface temperature, sulphate is reduced to sulphide by anaerobic bacteria that fulfill their energy needs by carbon oxidation with sulphate reduction rather than molecular oxygen, as follow:

$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO^{3-}$ (Equ. 1)

That reaction provides reduced sulphur for metal precipitation as well as alkalinity that can be of great value when sulphate reduction is used for the treatment of acid drainage (Germain et al., 2000). CH_2O in Equation 1 is a gross description of average organic matter. Sulphate reducing bacteria prefers glucose, provided more or less efficiently by the decay of straw, peat, manure, sawdust, composts and other organic substrates by various bacteria consortiums and enzymes, and by hydrolysis (*e.g.* Waybrant et al., 1997; Borek et al., 1995; Eger et Wagner, 1995). Given their availability at low cost and their proven usefulness at the East Sullivan Site (Germain et al., 2000), various types of old and recent barks were selected for an investigation of their actual and future performance with respect to sulphate reduction. Tests were carried out with water-saturated columns fed at different rates with a synthetic solution of Wood Cadillac waters.

A schematic view of the experimental set up is provided in Figure 1. A HDPE reservoir kept under nitrogen atmosphere and fitted with a siphon contains the synthetic solution. Single- and multi-channel peristaltic pumps feed sixteen, 10 cm i.d., ABS columns. Each column contains a 2 cm bed of 3/16" HDPE beads at the base, a 40 cm interval of < 3 cm barks, and a 6 cm upper compartment filled with similar beads, with a sampling port. The overflow of each column is collected for actual discharge measurement.

Bark composition

All bark samples come from wood waste piles of the Val d'Or area (Table 1). All samples were at least 5 years old, in order to avoid a bias from strongly reactive, but ephemeral components associated to young material. The set of columns features barks from coniferous and mixed coniferous-deciduous trees that have undergone long and short aerobic oxidation, and anaerobic degradation in water saturated and non-saturated milieus, below sewage sludge conditioner or not. Three samples were run in duplicate and one without sulphate in the feed solution, as a quality control. One was sieved into a fine (< 8 mm) and a coarse fraction (8-30 mm) to assess the importance of size. One contained about 5 % (w.) of a slow release fertilizer (10 % N total; 2 % P_2O_5; 4 % K_2O; 0.5 % Fe; 2 % S; 7 % O.M.). A commercial peat moss sample was added for the sake of comparison. Barks were added and compacted 800 cc at a time, with 30 cc of inocula between each addition (anoxic, organic, St. Lawrence River sediments).

Solution compositions and flow rates

Progress of tests is summarized in Table 2. Operating conditions were defined after several weeks spent on testing and adjustment of the flow lines. For the experiment, peristaltic pumps were operated at fixed speeds over regular intervals, within 24 h cycles. The initial flow rate was multiplied by two, and afterwards by four, in order to vary the residence time. Accordingly, sampling intervals were divided by two and by four. This way, data were obtained after circulation of similar pore volumes of solution trough out the experiment. About 2 L of solution was circulated during each sampling intervals (4 L with single-channel pumps), that is, about 2.4 pore volumes, assuming an effective porosity of 0.25 (4.8 PV with single-channel pumps). Actual flow rates were monitored by weighing effluents recovered at the outlet of each column (Figure 2). Columns were exposed to roughly similar amounts of waters.

Synthetic solutions (Table 2) were made with boiled spring water and transferred to reservoirs under N_2 pressure immediately after the addition and dissolution of standard salts. A Postgate C solution (Barton and Tomei, 1995) was used to stimulate bacterial growth for several weeks during the flow line adjustment. A synthetic Wood Cadillac solution without any arsenic or heavy metals ("SO4") was used for six weeks to gather analytical information on the implementation and stabilization of sulphate reduction. It was replaced by an "As500" solution, identical to the previous one but with 500 ppb As, 200 ppb Pb, and 500 ppb Zn. It was replaced by an "As1000" solution with

1000 ppb As, 400 ppb Pb and 1000 ppb Zn, since removal was very high. A separate reservoir with a "SO4 free" solution, identical to As500 and As1000 solutions, but without sulphate, was used with one column to determine to what extent sulphate reduction and arsenic removal were linked.

Sampling and analyses

pH, Eh, alkalinity and SO_4^{2-} were measured at seven days interval at the initial flow rate, then at 3-4 days intervals when it was doubled, and finally at 2 day intervals when increased fourfold. Multi-element analysis was added up as soon as the As500 and As1000 solutions were used. In all cases, samples were extracted from sampling ports with 60 cc syringes and filtered straight away on a 0.45 µm membrane. pH and Eh were measured immediately with an Orion 250A potentiometer fitted with Triode 91-07 BN and 96-78 BN electrodes, respectively. Alkalinity was obtained without delay by end-titration to pH 4.5 with HCl 0.1 N on a Mettler DL-25 automatic titrator with a DG 111-SC electrode (Greenberg et al., 1992). Sulphate concentrations were measured within 24 h with a Technicon Autoanalyser I (methylthymol blue method; Greenberg et al., 1992). Multi-element analysis was performed later by ICP-AES with an Optima 3000 on 18 mL aliquots acidified with 2 mL HNO_3 (Aristar grade). All samples were kept at (4ºC) when not under analysis.

Post–experience leaching

At the end of the test, three columns were selected for an acid leach, in order to check the stability of the arsenic removed from the solution. One column contained peat moss (high specific area), one fertilizer (enhanced performance during testing), and one was "normal" (0-8 ox.). Leaching proceeded at 600 mL/h, using successively pH 3 (day 1), pH 2 (day 2) and pH 1 (day 3) HCl solutions. Volume and pH of effluents were measured after each 0.5 PV. Each column was sampled 9 times for multi-element analyses between 1 et 2.5 PV. The leaching was stopped when the pH of the effluents was < 2.

Results

Results are summarized in Figure 3 for sulphate, arsenic, pH and alkalinity. Figure 4 show how these parameters vary when sulphate reduction is enhanced by addition of a fertilizer, or inhibited when a sulphate-free solution is fed to the column. First order logarithmic regression lines are provided for better visualization. Actual concentrations in the influent appear near the left axes of the diagrams. Sulphate values are close to the target concentration. Arsenic is about half the expected values, probably as a result of a lost to the reservoir walls by adsorption. Other data will not be discussed here. Lead and zinc were very low even in the inflow, likely because their salts were very difficult to dissolve. Some concentrations were found to be in higher in the outflow than in the inflow, especially in the initial steps, *e.g.* K, Na, Mg, and even Fe, Mn and P (not added!). These were likely dissolved from aerosols carried onto the wood piles.

Sulphate reduction

Sulphate reduction is favoured by low flow rates, that is, long residence times. Efficiency vary according barks type, age and degree of previous involvement in aerobic oxidation:

- old organic substrates (Victoria Pine, 4th Street, peat moss) do not perform as well as more recent coniferous barks (C6 ox. and non ox.), with about 20 % sulphate removal *vs* 30-35 %, both at 50 mL/h;
- barks with a deciduous component are better at sulphate reduction, except if previously exposed to direct aerobic oxidation; removal at 50 mL/h is around 70-75 % for C7 and 0-8 non. ox., whereas it is only a little more than 20 and 30 % for C7 and 0-8 ox.;
- amongst the oldest barks (1960's), those that were under constant oxidation (Victoria Pine) do not perform as well as those subjected to intermittent water saturation (4th Street);
- coarse barks are slightly better performer than fine barks in sample 0-8 (about 80 *vs* 70 % removal), a conclusion against what would be expected from their surface specific area; in that case, sawdust proportion, with a lower reactivity, likely offsets size advantage;

- as expected, sulphate removal is greater when sulphate reduction is stimulated by nutriments (Figure 4).

pH and alkalinity

Bark degradation releases organic acids that can modify the pH and alkalinity of a solution, and sulphate reduction is a process that increases alkalinity (Equation 1). Long residence times favour sulphate reduction and the release of organics to the solutions. pHs are thus lower and alkalinities higher at slow rate of circulation (Figure 3). When little or no sulphate reduction goes on, pH undergoes a stronger decrease, whereas alkalinity of inflow is in no way increased, but more or less preserved (Figure 4). When sulphate reduction is stimulated, pH does not decrease as much, whereas alkalinity is much higher. The peat moss column is a notable exception in the results obtained. It is the only one in which alkalinity decreases, despite on-going sulphate reduction. In all columns, some alkalinity produced by sulphate reduction is always added to the alkalinity of the feed solution, and it is not clear to what extent that sulphate reducing alkalinity was used to counteract at least partially the decrease of pH related to organic acids. In the peat moss column, however, net consumption tapping also the alkalinity of the feed solution suggest that alkalinity played its role in preventing a further decrease of pH.

The rise of alkalinity is proportional to sulphate removal. It follows that the rise is the lowest with the old barks (Victoria Pine, 4th Street), with an increase of overall alkalinity at best comparable with recent coniferous barks (C6 ox. and non ox.), with little (1.5X) or no increases (1.0X) at 50 mL/h. Non oxidized, mixed composition, barks (C7 and 0-8 non ox.) have a greater impact on alkalinity, with increases by factors over 2.3X, up to 4X. Again, their oxidized counterparts (C7 and 0-8 ox.) are not as good in rising alkalinity (1.5X and 1.9X at 50 mL/h). Finally, the 4th Street barks are doing better than the Victoria Pine one's, amongst very old barks.

pH decreases from 7-8 in the inflow to 6 in the outflow of most columns. The lower pHs are reached with the older barks at low flow rates, again with a small edge of 4th Street bark (6.0) over Victoria Pine's (5.8). C6 ox. and non. ox. (coniferous barks) are as much sensitive to pH than old barks, again with a small advantage for the non oxidized sample. Ranking of other samples are not as easy as with alkalinity (*e.g.* C7 ox. *vs* C7 non ox.) and higher pH at 6.6-6.8 values are clearly the fact of higher flow rates.

Arsenic removal

Arsenic removal varies between 85 and 95 % except at high flow rates, for barks that proved to be less efficient in sulphate reduction (Figure 3; Victoria Pine barks: old; 0-8 non ox. fine: high sawdust proportion). Arsenic removal also occurred in a column to which no sulphate was provided (Figure 4). In that case, decreasing amounts of SO_4^{2-} were measured in the outflow, suggesting dissolution of aerosols originally mixed with the barks. Since As was present at the few hundred of ppb level and SO_4^{2-} at the ppm level, there were enough sulphides to precipitate As, if precipitated as sulphide. At the opposite, increased sulphate reduction by fertilizer addition did not help to remove more arsenic, compare to the "normal" column (Figure 4).

Acid leaching to pH 2 suggests that arsenic was removed as As_2S_3, or as another fairly stable phase. Only one out of 27 analyses shows As above detection limit (0.06 ppb, with d.l. = 0.04 ppb). Amounts of As in the columns were calculated from volume of solutions circulated and As determinations in inflow and outflow. If the actual As concentration in the leached solution is equated to the detection limit, a maximum of 5 to 10 % of the arsenic could have been mobilized without being detected.

Biofilter design

Results obtained in the lab show that arsenic can be removed by sulphate reduction at a rate that vary with bark composition and time of residence within the column. The next step was to use the hydraulic and kinetic data to design a biofilter that would allow the Wood Cadillac water meet the criteria required for a safe disposal in the environment. A more complete discussion is available in Isabel et al. (2000).

The hydraulic conductivity K could be estimated from hydraulic heads measured downstream and upstream of the columns and from their discharge. The average of 13 determinations was 8.1 X 10^{-3} cm/s, which compares well with an average of 1.9 X 10^{-2} cm/s obtained in the field at East Sullivan (D. Germain, personal communication). For design purpose, K was assumed to be 1 X 10^{-3} cm/s. Pore water volumes were fixed in the experiment (3 242 cc of barks with a 23 % kinetic porosity: 745 mL). Dividing by the discharge gave residence times that could be associated with arsenic concentrations in the outflows. Aiming to an outflow with 14 µg/L As (criteria for groundwater discharging into a river or a creek), it was found that this objective could be met by many type of barks with a residence time of 25 h. As expected, those with a mixed composition (coniferous + deciduous: C7, 0-8) proved to be the best substrates. Coniferous barks were found interesting if evolved in an intermittent saturate milieu (4th Street). Otherwise, they were marginally adequate or inadequate (C6). Deeply oxidized, old, coniferous barks (Victoria Pine) could definitively not meet the requirements.

The biofiltre was scaled for these parameters and designed to allow continual water saturation (to keep anoxic conditions), bypass of running water upstream of the tailings (to reduce the load), full treatment of water in normal water conditions (assuming runoff and infiltration equal to 70 % of a 870 mm yearly precipitation, over 38 ha), bypass of excess water during high water periods (little or no contamination in theses conditions), vertical flow (low topography did not allow a horizontal design). A 50 X 57 m biofilter with a thickness of 1 m was found to meet these requirements, built and put under observation (Germain and Cyr, this volume).

Discussion

Studies directed towards compost and farming have soon recognized that rates of decomposition of wood vary according to tree species, age, part, and so forth, but that, overall, rotting proceeds more readily with deciduous than with resinous trees (Allison et Klein, 1961; Allison et Murphy, 1963; Bollen et Glennie, 1963). Our results converge with that observation. Barks with a mixed composition (0-8, C7) showed a better performance than younger coniferous barks (C6) at sulphate reduction, likely because they were able to decompose more easily. Deciduous wood waste is a better choice for a biofilter. Results obtained with more or less degraded coniferous barks suggest that sulphate production can undergo efficiently for several years.

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Table 1. Summary of main bark characteristics used for tests.

Sample[1]	*Type of barks*	*Date of deposition*	*Sampling depth (cm)*	*Sample environment*	*% <3 cm*	*Column number*	*Notes*
peat moss	-	-	-	-	100.0	21	
Victoria Pine	coniferous	1956-66	20-40	aerobic	69.2	1	dupl. of 2
Victoria Pine	coniferous	1956-66	20-40	aerobic	69.2	2	dupl. of 1
0-8 ox.[2]	mixed	1990	0-20	aerobic	94.0	16	
0-8 non ox.[2]	mixed	1990	60-80	anaerobic	98.1	12	fine fraction
0-8 non ox.	mixed	1990	60-80	anaerobic	98.1	13	coarse fraction
4th Street	coniferous	1966	20-40	±water sat.	98.5	10	dupl. of 9
4th Street	coniferous	1966	20-40	±water sat.	98.5	9	dupl. of 10
C6 ox.	coniferous	1992	0-30	aerobic	90.3	14	
C6 non ox.	coniferous	1992	150-160	anaerobic	89.7	5	dupl. of 6
C6 non ox.	coniferous	1992	150-160	anaerobic	89.7	6	dupl. of 5
C7 ox.	mixed	1985	20-40	aerobic	93.0	15	
C7 non ox.	mixed	1985	75-90	anaerobic	87.1	7	no SO_4 in feed
C7 non ox.	mixed	1985	75-90	anaerobic	87.1	8	
C7 sat.	mixed	1985	> 125	water sat.	75.7	4	
C7 non ox.	mixed	1985	75-90	anaerobic	87.1	19	with fertilizer

[1]: Sample locations:
Victoria Pine: la Vérendrye Park; 0-8, C6, C7: East Sullivan Site, C6 and C7 with sewage sludge over surface; 4th Street: Val d'Or

[2]: ox.: oxidized; non ox.: non-oxidized

Table 2. Composition of solutions fed to the columns.

Day	*Flow rate*[1]	*Feed solution*	*Solution composition*
<u>all columns:</u>			
8 weeks	irregular	Postgate C	see Barton and Tomei (1995)
1-18	1X	SO4	9.5 mg/L KCl, 61.8 mg/L Na_2SO_4, 101.4 mg/L $MgSO_4.7H_2O$, 212.6 mg/L $CaSO_4.2H_2O$, 139.7 mg/L $CaCl_2$
19-25	shut down	-	
<u>all columns but 7:</u>			
26-38	1X	As500	as above plus 2.1 mg/L $Na_2HAsO_4.7H_2O$, 0.3 mg/L $Pb(NO_3)_2$, 1.0 mg/L $ZnCl_2$
39-45	1X	As1000	as above but 4.2 mg/L $Na_2HAsO_4.7H_2O$, 0.6 mg/L $Pb(NO_3)_2$, 2.1 mg/L $ZnCl_2$
46-59	2X	As1000	
60-65	4X	As1000	
<u>column 7:</u>			
26-38	1X	SO4 free-500	9.5 mg/L KCl, 25.4 mg/L NaCl, 83.7 mg/L $MgCl_2.6H_2O$, 276.8 mg/L $CaCl_2$, 2.1 mg/L $Na_2HAsO_4.7H_2O$, 0.6 mg/L $Pb(NO_3)_2$, 2.1 mg/L $ZnCl_2$
39-45	1X	SO4 free-1000	as above but 4.2 mg/L $Na_2HAsO_4.7H_2O$
45-59	2X	SO4 free-1000	
60-65	4X	SO4 free-1000	

[1]: Actual flow rates averaged for multi-channel and single-channel pumps, respectively:
1X: 11.3 and 25.4 mL/h; 2X: 23.0 and 45.5 mL/h; 4X: 46.8 and 89.4 mL/h

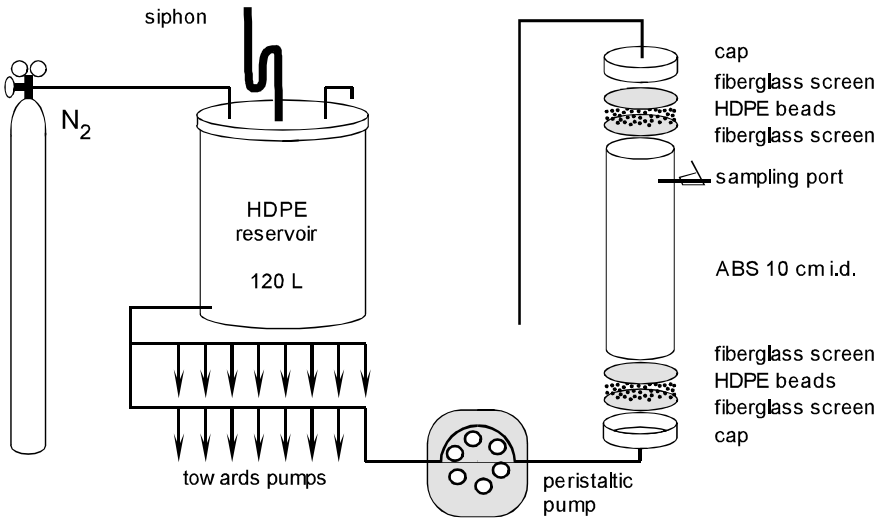

Figure 1. Experimental set up.

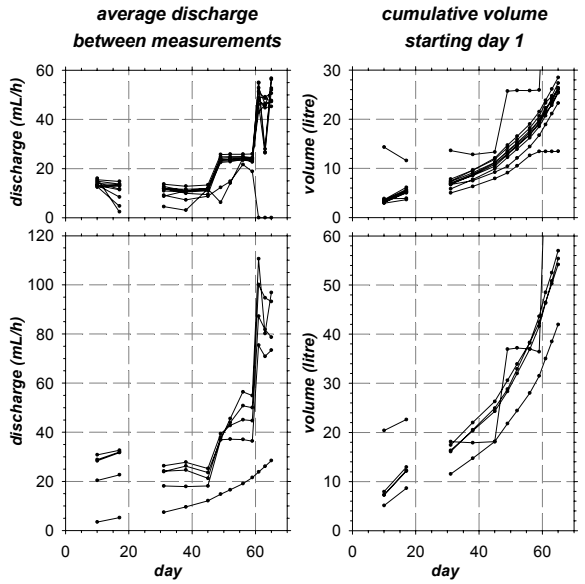

Figure 2. Variations of discharge and cumulative volume during the experiment. Top: multi-channel pump. Bottom: single-channel pumps.

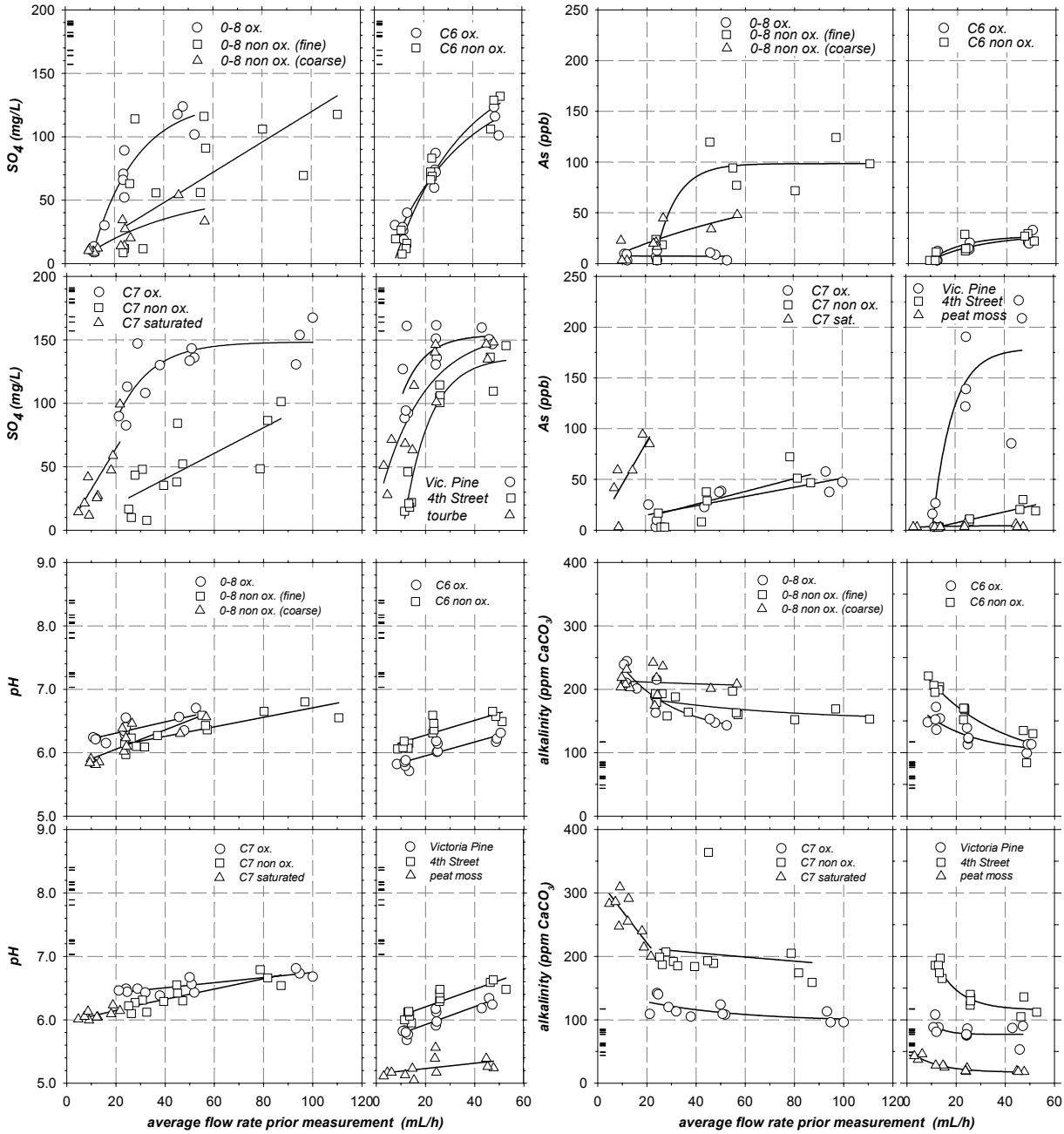

Figure 3. Variations of SO_4^{2-}, As, pH and alkalinity in the outflow, with respect to flow rates. Lines next to the ordinates are values obtained upstream of the columns.

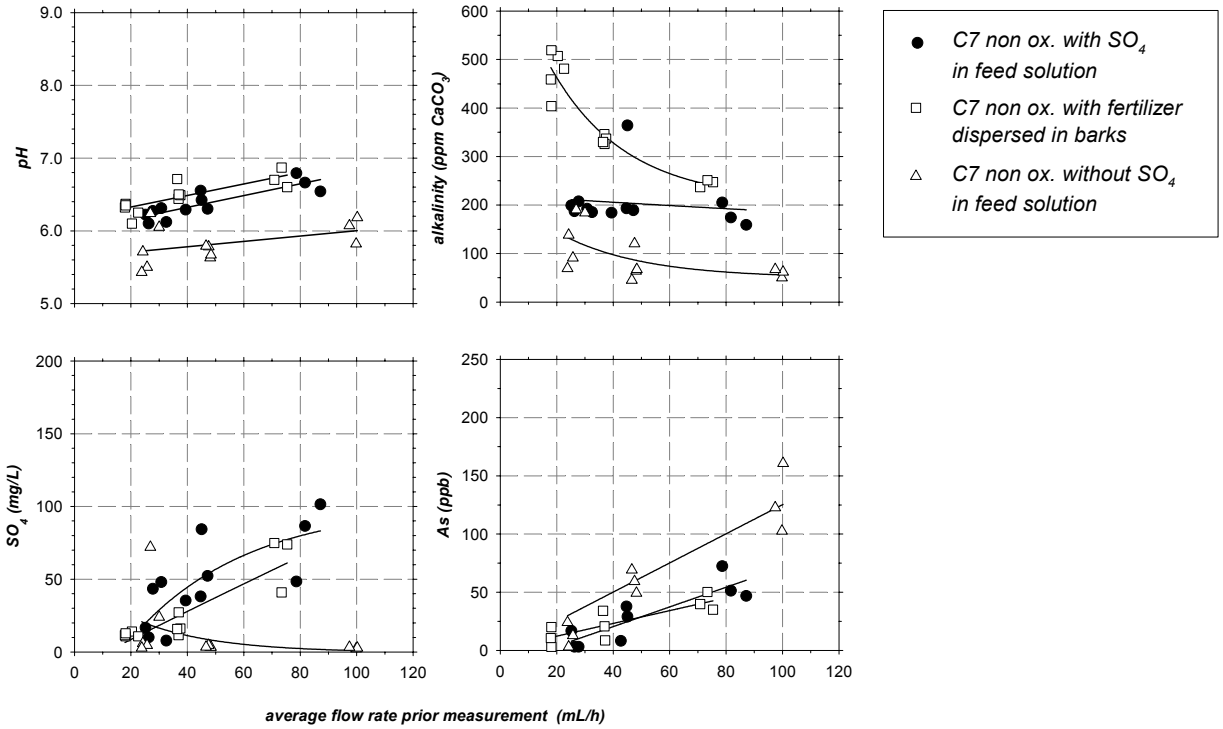

Figure 4. Variations of pH, alkalinity, sulphate and arsenic concentrations in the outflow, in conditions of enhanced and inhibited sulphate reduction, with respect to flow rates. SO_4^{2-} measured in sulphate-free column is ascribed to aerosols dissolution.