Treatment of Acid Mine Effluents Using a Wood-Waste Cover[1]

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Abstract

At the East Sullivan site, wood wastes covering the abandoned mine tailings impoundment prevent sulfide oxidation by creating an anoxic environment. The addition of coarse ligneous wastes and their high permeability favor infiltration, resulting in a water table rise that maintains most tailings under water saturation and thus provides an additional protection against sulfide oxidation. Moreover, high infiltration allows a more rapid flushing of acid prone groundwater generated prior to the cover placement, which could cause acid mine drainage over a long period of time. Finally, the pore-waters under the cover are characterized by a strong reducing potential, high alkalinity, and near neutral pHs. These conditions favor sulfate reduction and base metal precipitation as sulfides and as carbonates. Pore-water composition monitored from 1992 to 1998 showed a significant Fe^{2+} decrease, following cover placement. Thereafter, the restoration strategy capitalized on the alkaline and reductive properties of the waters underlying the wood-waste cover. An original treatment of acid effluents, based on the recirculation of water discharged around the impoundment through the organic cover, was implemented. In 2002, the recirculated water from May to October had a mean pumping rate of 240 m^3/h, for a total volume of 800 000 m^3. Data gathered near the dispersal zone from 2000 to 2002 show that despite the recirculation of acid water (pH ≈3), the pH decreases by only one unit from 7 to 6, during the recirculation period. However, alkalinity decreases from 800 to 100 mg/L-$CaCO_3$. Despite this decrease, the alkalinity is back up to 800 mg/L-$CaCO_3$ the following spring, thanks to sulfate reduction. Fe^{2+} concentrations are maintained below 2 mg/L. A wood-waste cover, besides limiting sulfide oxidation, can fill the role of alkaline reducing barrier for the treatment of these acidogenic waters, until a balance between acidity and alkalinity in the effluent is reached.

Limiting Acid Mine Drainage with Organic Covers

The possibility to use organic covers to prevent the oxidation of sulfidic mine tailings was proposed several years ago (Reardon and Poscente 1984, and references therein). In this type of cover, atmospheric oxygen is consumed by the oxidation of carbon, hence its absence in the interstitial gases coming in contact with the sulfides. The nature of the material used may vary. Forestry wastes have been laid down since 1984 at the East Sullivan site in north-western Québec. Pulp-and-paper-mill wastes have been used in Sweden (Broman *et al.*, 1991) and at the Eustis site in southern Québec (Cabral *et al.*, 1997). Reardon and Moddle (1985), Pierce (1992), and Pierce *et al.* (1994) discuss the suitability and the laboratory performance of such materials as peat moss or municipal-waste composts.

Wood wastes are *a priori* an interesting material for organic-cover construction, since forest industry is often active in mining areas. On a conceptual basis, such a cover presents several advantages over other types of cover or organic substrates:

- placement of such a cover does not perturb the natural milieu; instead, it is recycling industrial waste;
- it implies only low construction costs, if readily available;

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- its physical and chemical properties are not affected by the growth of vegetation;
- wood wastes are less prone to react, less easy to dissolve, and without pathogenic microorganisms, compared to human or animal wastes.

The sole laboratory test that we are aware of was not conclusive. Acid production was 30% higher in a test column of sterile rocks overlain by wood waste than in a reference column (Payant *et al.*, 1995). These results are clearly imputable to the thin layer of wood waste used (15 cm, uncompacted), insufficient to decrease the oxygen flux, but sufficient to act as a thermal insolent and improve the efficiency of sulfide oxidizing *Thiobacillus* colonies. On the other hand, the East Sullivan site, near Val d'Or, is the locus of a full-scale experiment where the cover functionality in term of oxygen consumption is well demonstrated (Tassé *et al.*, 1997).

Besides their oxygen-consuming attributes, Tassé *et al.* (1997) recognized in the wood wastes several physical and chemical properties that could be put at work in a mine site rehabilitation. The geochemical environments below such a cover are reducing and alkaline. The reactions taking place in such organic rich environment are analog to those occurring in better known constructed wetlands and reactive-walls (*e.g.* Wildeman *et al.*, 1992, Waybrant *et al.*, 1997). On a conceptual basis, acid and acidic residual waters can be treated via recirculation into that milieu. Moreover, recirculation through highly permeable wood wastes increase water infiltration, raise the water table, and allow to purge more rapidly acid-prone groundwater generated prior to organic cover placement.

Forestry wastes laid down over the East Sullivan mine tailings now cover about 85% of the 136 ha impoundment. The tailings pile, its wood-waste cover, and the acid and heavy metal-rich pore and surface waters have been surveyed since the early 1990s. Germain *et al.* (2000) have presented the early response of the organic cover as a biofilter. While this paper reviews and integrates data regarding the cover performance and its capacity to treat acid and metal rich waters through recirculation from 1998 to 2002.

The East Sullivan Mine Tailings and the Transition to a Non-Acid Drainage

The East Sullivan mine tailings lie 6 km east of Val d'Or, Québec (Fig. 1). Cover placement started in 1984, 18 years after mine closure. The type of forestry wastes used varies according to time and sector of deposition (Table 1).

The efficiency of the wood wastes cover as a functional oxygen barrier has been demonstrated. However, the interruption of sulfide weathering either by an organic barrier or by some other oxygen-proof cover does not imply an immediate cessation of acid mine drainage. Acid-prone waters generated prior to cover placement must first be flushed out from the tailings. In tailings piles, acid is generated in the near surface by pyrite oxidation, either by atmospheric oxygen (Eq. 1) or by ferric iron (Eq. 3). Oxidation and hydrolysis of iron produces acid as well (Eq. 2 and 4). However, the kinetics of reaction 2 is very slow in acid conditions (Stumm and Morgan, 1996), so that Fe^{2+} can migrate from the near surface to an anaerobic environment. At East Sullivan, acid generated near the surface is neutralized by interactions with the mineral medium in the saturated zone, so that pH increases along the flow path. It follows that rapid Fe^{2+} oxidation (Eq. 2) is kinetically possible at emergence, when O_2 is available again, with hydrolysis and production of acid (Eq. 4). This mechanism can continue well after the placement of an oxygen barrier. In fact, it is problematic until a balance between acidity and alkalinity in the effluent is reached.

$$FeS_2 + {}^{7}/_{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$
$$Fe^{2+} + {}^{1}/_{4}O_2 + H^+ \longrightarrow Fe^{3+} + {}^{1}/_{2}H_2O \quad (2)$$
$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{3+} + 2SO_4^{2-} + 16H^+ \quad (3)$$
$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \quad (4)$$

Table 1. Main characteristics of the mining and forestry wastes

Mine tailings:			
metals extracted	Cu, Zn (Au, Ag)	*period of accumulation*	1949-66
sulfide concentration	3.6% S	*tonnage*	15 Mt
sulfide mineralogy	FeS_2 ($Fe_{1-x}S$, $CuFeS_2$, ZnS)	*area*	1.36 km^2 (+0.68 km^2 of spreading)
acid generating potential	108.9 kg $CaCO_3$/t	*morphology*	4-5 m plateau
acid neutralizing potential	4.1 kg $CaCO_3$/t	*thickness*	2-14 m

Organic wastes:			
	northwest sector	*south sector*	*northeast sector*
accumulation period	1984-92, then at low pace	since 1992	since 1999
species	deciduous dominant over conifers	mainly conifers	conifers and deciduous
types of waste	bark fragments, logs, presswood waste, mostly overlain by sewage sludges	bark fragments, sawdust, and logs	bark fragments
thickness	0.2 to 6 m (pre-1990) and 2 m (post-1990)	≈ 2 m	≈ 2 m

Basic acidity/alkalinity balance allows some predictions about the pH behavior for a given pore water discharged around the impoundment. Samples collected under the oldest parts of the cover (pre-1992, North sector) generally present no threat –high alkalinity and low Fe^{2+} (Fig. 2). Elsewhere, most acid prone samples are located next to spigotted dikes and former dikes, now enclosed in finer tailings. They can also be located in more central parts, in tailings directly poured out from the mouth of carrying pipes. These locations correspond to zones of high hydraulic conductivity, where O_2 diffusion favors or has favored high rates of alteration (C20, fig. 2). Alteration and acid generation is also enhanced near margins, because the vadose zones are deeper than within the impoundment, allowing deeper weathering. Short transport times and lengths are also prejudicial to neutralization and increase in alkalinity.

The Concept of Water Treatment by a Wood-Waste Cover

A forestry-waste cover can be profitably used for the management of acid prone groundwaters flushed after cover placement. Actually, it features the essential geochemical characteristics driving passive treatment systems such as constructed wetlands and other reducing barriers, in which redox reactions help to improve the general effluent quality (*e.g.* Wildeman *et al.*, 1992; Blowes *et al.*, 1995; Waybrant *et al.*, 1995). In those anoxic environments, sulfate-reducing bacteria, in the absence of molecular oxygen, secure their energy needs by oxidizing organic compounds, using the sulfur of sulfate as the terminal electron acceptor (Eq. 5). Metals are precipitated by reduced sulfur (Eq. 6), and the resulting acid is neutralized by the alkalinity produced by sulfate reduction (Eq. 7).

$$SO_4^{2-} + 2CH_2O \longrightarrow H_2S + 2HCO_3^- \quad (5)$$

$$Me^{2+} + H_2S \longrightarrow MeS + 2H^+ \quad (6)$$

$$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O \quad (7)$$

where Me represents Fe, Ni, Cu, Co, Zn, Cd, *etc.*

At East Sullivan, the characteristic H_2S smell of reduced sulfur was noted at some observation wells, which is clear evidence that sulfate reduction is going on. Alkalinity, below the wood-waste cover, reaches considerable values, up to 1000-1500 mg/L-$CaCO_3$ (Fig. 2). Alkalinity values in this range correspond to dissolved inorganic carbon (DIC) between 120 and 270 mg/L-C, indicating a carbonate alkalinity (Germain, 2000). Furthermore, water in equilibrium with CO_2 partial pressure of 20% and 40%-vol observed at various locations has an alkalinity of 1300-1500 mg/L-$CaCO_3$ at pH 6.

The alkaline and reducing properties observed below the wood waste cover at East Sullivan are essentially those of a constructed wetland. In the

same way, reduction of sulfate to sulfide in these geochemical conditions can provide the counter-ions required for the precipitation of iron and other metal sulfides. A treatment system similar to a constructed wetland was thus at hand, and waiting to be put at work. This was done by simply recirculating the acid rich effluents collected around the impoundment through the wood waste cover.

Recirculation System and Its Efficiency

Implementation

At East Sullivan, the effluents around the impoundment are collected into four reservoirs: North (70 000 m^3), West (30 000 m^3), East (250 000 m^3), and South (900 000 m^3) (Fig. 1). The recharge rates, in m^3/d, are, for North: 1170; West: 430; East: 6600 (South: currently not available). The high rate for the East reservoir reflects the fact that it drains most of the impoundment (see flow directions, Fig. 1).

The water from the North reservoir flows into the West reservoir. Pipes are connected to the outlets of the West and East reservoirs and water is directed to a pumping station at the southern end of the site. There, water from either West, East or South reservoirs can be pumped back over the organic cover, or is allowed to flow by gravity into the natural environment (Fig. 1). The dispersal zone, 120 m long perforated pipe, is located over the oldest, mid-eighties, part of the cover. Table 2 indicates the average pumping rates and total volumes of water treated from 1998 to 2002. Figure 3a shows the measured pumping rates from 2000 to 2002.

Water Quality at Feed-Pipe

pH, alkalinity, iron and sulfates concentrations in feed-waters are shown in Figure 3. Since 2000, the first reservoir being pumped in the spring is the East one until its quality meets the criteria shown on Table 3, then the South one is pumped until the end of October. Since the beginning of the recirculation operation, the maximal concentration of Fe_{total} has decreased from over 400 mg/L in 1998 to 70 mg/L in 2002. For the past three recirculation periods, pH was below 3.5 most of the time (Fig. 3b).

Table 2. Average pumping rate and total volume of water treated

Year	mean pumping rate (m^3/d)	volume (m^3)
1998	2500	420 000
1999	3750	630 000
2000	5390	650 110
2001	5928	741 530
2002	5760	798 555

Table 3. Main water quality criteria

Inorganic parameters	*maximum concentration*
Cu	0.30 mg/L-Cu
Ni	0.50 mg/L-Ni
Pb	0.20 mg/L-Pb
Zn	0.50 mg/L-Zn
Fe(total)	3.00 mg/L-Fe
pH	between 6,5 and 9,5
Organic parameters	
Chemical oxygen demand	<100 mg/L-O_2
Biological oxygen demand	<50 mg/L-O2
Phenols	<0.05 mg/L

Efficiency of Water-Treatment System

The efficiency of the biofilter can be assessed by comparing feed-water descriptors to those of groundwater collected in a nearby observation well, C3-p4. That well is located next to the dispersal, near the edge of the cover, at 3.1 m depth (Fig. 1). It is thus safe to assume that evolved feed-waters flowed through that station, in a setting where the capacity of the system was pushed more than elsewhere to its limit. Residence time is estimated at 10 days/1 m, vertically, in its vicinity; the parameters used are measured *in situ* hydraulic conductivity of 6E-5 m/s, and vertical hydraulic gradient of 0.1 when the system is in operation. The porosity is assumed to be 0.5. Thus, it takes about 30 days for feed waters to reach this observation well. That residence time was sufficient to decrease Fe^{2+} concentrations from more than 200 mg/L to less than 1.5 mg/L (Fig. 3d). A similar residence time (40 days) allowed a decrease from 375 mg/L-Fe^{2+} to less then 5 mg/L, in batch experiments using deciduous and coniferous wastes as porous media (Tassé and Germain, 2002).

From 1998 to 2002, the pore waters quality at C3-p4 also improved over time with respect to ferrous iron, as noted for the feed-waters (Fig. 3d). More specifically, the average Fe^{2+} concentration decreased from 28.2 mg/L in 1998 to less then 1.5 mg/L in 2002. The fraction of ferrous iron removed increased progressively from 86% to 97% from 1998 to 2001 (Table 4). The increased efficiency of the biofilter over time is likely due to the establishment of bacteria colonies responsible for sulfate reduction.

Table 4. Average Fe^{2+} present in feed waters and in pore waters at observation well C3-p4

	Average Fe^{2+} (mg/L)		
Year	Feed Waters	C3-p4	% removed
1998	201.8	28.2	86
1999	93.3	5.9	94
2000	39.1	<1.5	n.a.
2001	47.3	1.6	97
2002	3.6	<1.5	n.a.

pH was always near neutral in the five years surveyed, despite the more than often acid feed waters. With a feed water less than pH 4.5 over the entire 2001 season, and a water volume of more then 740,000 m^3 pumped over the wood waste cover, the pH of the pore waters decreased by only one unit during that time, from 7 to 6. This is because pH and alkalinity are two interrelated parameters: if an acid is added to an alkaline solution, pH is preserved while alkalinity is consumed. In the present case, alkalinity dropped from 835 to 100 mg/L-$CaCO_3$ that same year. Over a period of 169 days, that represents a rate of -4.4 mg/L-$CaCO_3$ per day. In the previous year (2000), a similar behavior was observed: pH decreased by one unit and alkalinity dropped from 735 to 231 mg/L over a period of 132 days, which represents a rate of -4.1 mg/L per day. Despite these drops, alkalinity went back to 800 mg/L the following spring. The re-establishment of alkalinity outside the recirculation period can be due to:

- the migration of alkaline waters located upstream of the dispersal zone, and/or
- *in situ* alkalinity generated by on-going sulfate reduction (Eq. 5), and/or
- *in situ* alkalinity associated to the alteration of organic components, for instance into humic and fulvic acids.

The relationship between alkalinity and the sulfate reduction is reflected in the response observed at C3-p4 on July 17, 2002. Since the residence time is 30 days, the difference between the sulfate concentration of the feed waters on June 17, 2002 and that at C3-p4 is 410 mg/L (Fig. 3e), which corresponds to a gain in alkalinity of 427 mg/L-$CaCO_3$ (Eq. 5). Part of this alkalinity, about 50 mg/L-$CaCO_3$, was consumed in order to rise the pH from 3.0 to 6.5. Thus, the resulting alkalinity is estimated to be in the range of 377 mg/L-$CaCO_3$. The observed alkalinity is in fact 360 mg/L indicating that most alkalinity is in the form of carbonate and is coming from sulfate reduction.

Distribution of alkalinity, Fe^{2+}, and SO_4^{2-} along a North-South cross-section of the impoundment in July 2002 is shown in Figure 2. Fe^{2+} is a key parameter for water quality, since its oxidation and hydrolysis are responsible for the acid and mine drainage. An important Fe^{2+} plume, with concentration up to 15 000 mg/L, grossly matches a SO_4^{2-} plume, as expected from pyrite oxidation. A lack of similarity in the northern part of the cross-section is likely related to siderite precipitation that decreases Fe^{2+}, and possibly jarosite and melanterite dissolutions that increases SO_4^{2-}, as suggested by calculations of saturation indexes (Germain, 2000 and 2003).

Conclusions

A cover of forestry wastes presents, from the outset, all the advantages attributed to organic covers in relation to other types of cover. It needs a less fragile and less complex infrastructure than inorganic covers; it is a potential substitute in the absence of suitable inorganic material in a given restoration area; it does not disturb the natural environment, since it uses industrial waste rather than natural materials. Coarse ligneous wastes favor higher infiltration and a water table rise, which plays the role of a "wet cover". This also allows a more rapid flushing of acidogenic groundwater. Furthermore, a wood-waste cover, besides limiting sulfide oxidation, can fill the role of an alkaline reducing barrier for the treatment of these acidogenic waters, until a balance between acidity and alkalinity in the discharged water is

reached. Such a system holds several advantages over conventional constructed wetlands, which are driven by the same geochemical processes: it is *a priori* less sensitive to hydrogeologic and vegetative cycles that affect wetlands, because anaerobic conditions can persist despite strong irregularities in influent and climatic conditions; contact time can be long relative to a constructed wetland, and levels of oversaturation solution are likely to be attained and maintained.

Since 1998, acid and acidogenic waters collected around the East Sullivan impoundment are recirculated through its organic cover. The treatment is based on sulfate reduction and alkalinity production favoring the precipitation of Fe^{2+} as sulfur and carbonate. The predominance of the precipitated form still needs to be determined. Nevertheless, the treatment is getting more efficient with time, as shown by the amount of Fe^{2+} being removed in an observation well near the dispersal zone, passing from 86% in 1999 to 97% in 2001. The system can also neutralize acid waters, pH observed in eight nearby observation wells being maintained above 6, despite acid feed water. Alkalinity is mainly one of carbonates generated from sulfate reduction and from oxidation of organic matters. Results also show that recirculation increases the flushing rate of acidogenic waters.

It is thus clear that an organic cover not only can act as an oxygen barrier, but can also be integrated in a strategy for an efficient treatment of transient acidogenic waters.

Acknowledgments

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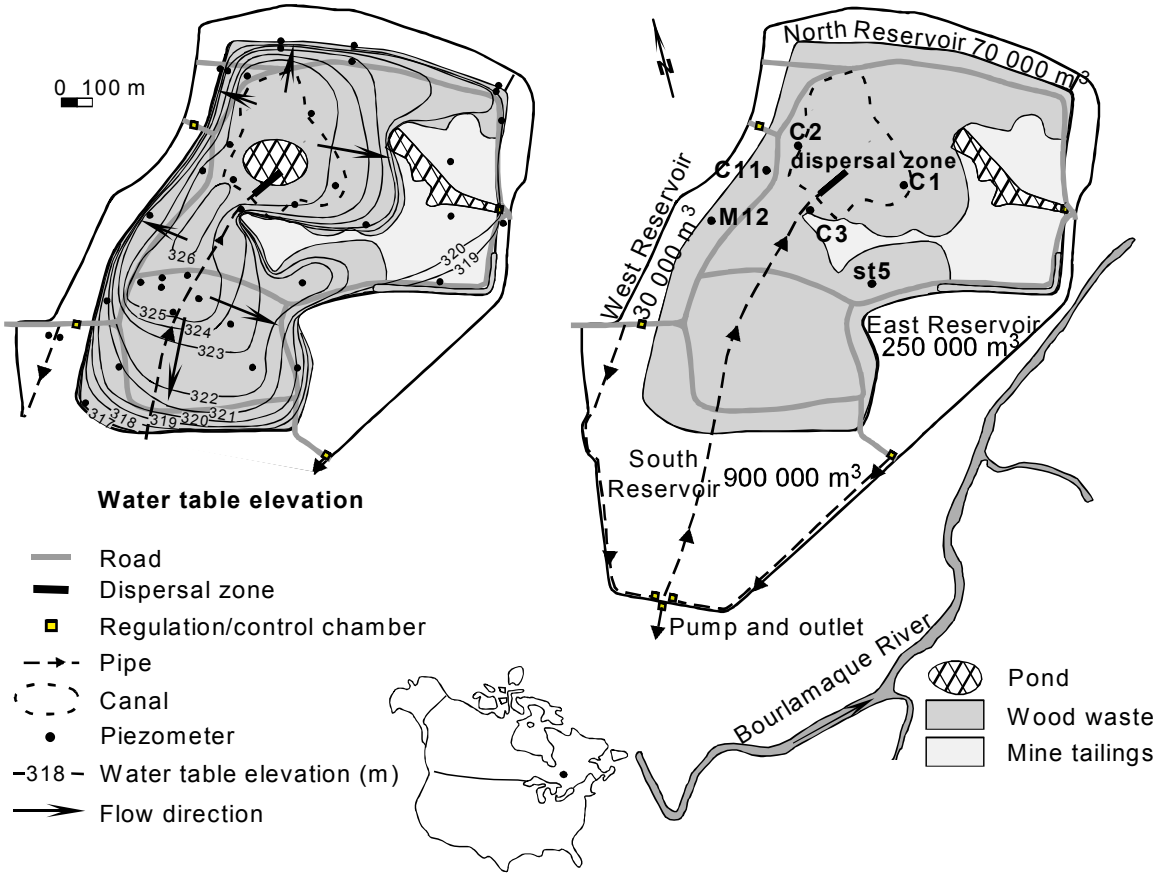

Figure 1. The East Sullivan tailings impoundment with water table elevation when the recirculation is in operation, and locations of observation wells and dispersal zone

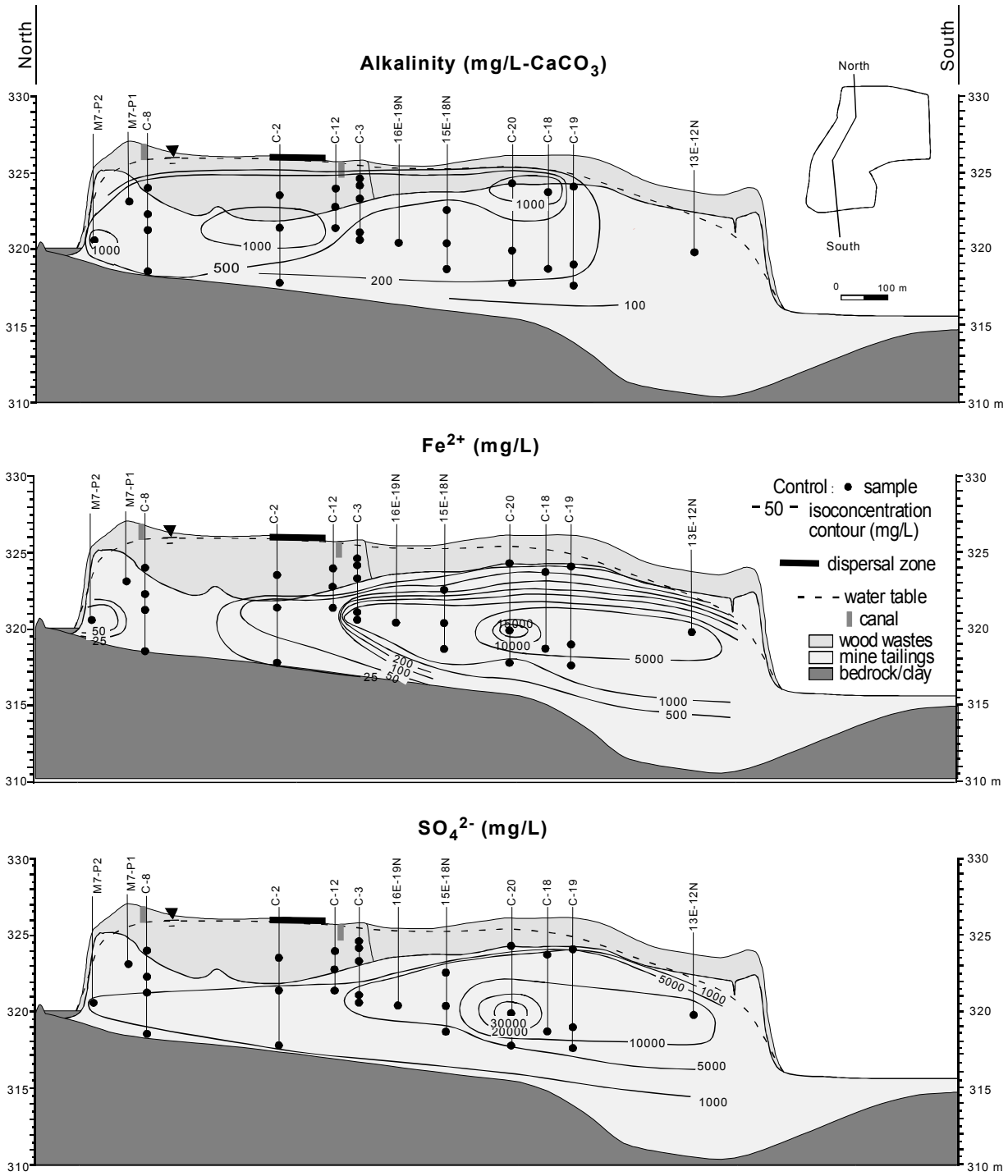

Figure 2. Alkalinity, Fe^{2+}, and sulfate distributions along a north-south cross-section in July 2002

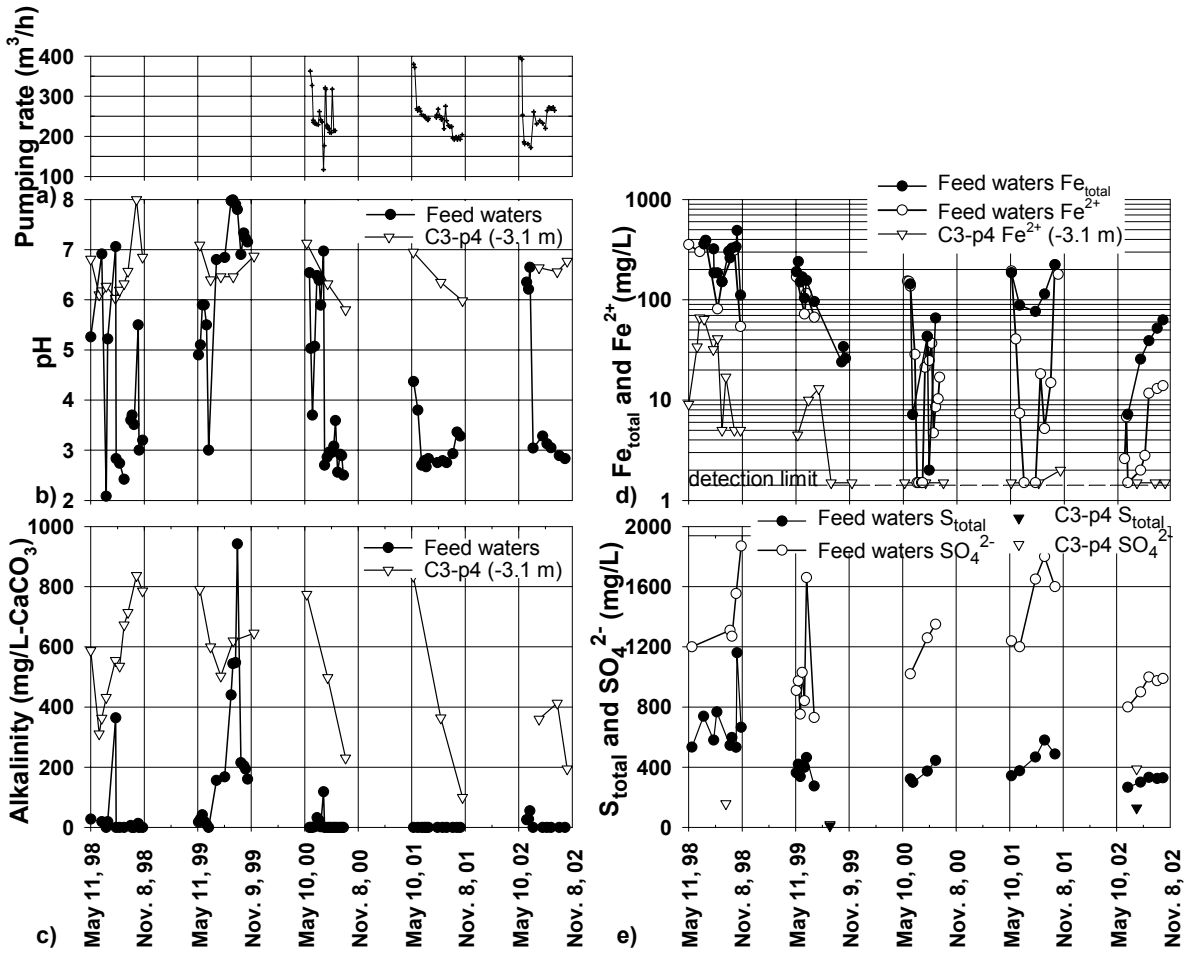

Figure 3. Pumping rate (a) from May 1998 to October 2002, and feed-waters and groundwater quality at station C3-p4 : (b) pH , (c) alkalinity, (d) Fe^{2+}, and (e) sulfates