Evaluation of biofilter performance to remove dissolved arsenic: Wood Cadillac*

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Abstract

The Wood Cadillac mining site, in north-western Quebec, is an important source of arsenic contamination. The arsenic-rich effluent is treated through a reductive biofilter, which allows arsenic to precipitate as a sulphide (likely As_2S_3). The top-fed biofilter, built at the end of 1999, is 50 m x 57 m by 1 m thick. The reducing conditions are provided by the decomposition of yellow birch bark chips. At the outlet, dissolved arsenic was maintained below 57 µg/L during the entire period investigated, which is May 2000 to October 2002, except June 20th 2001 (93 µg/L). Relative to mean input values of 103, 227, and 168 µg/L in 2000, 2001, and 2002, arsenic concentrations were removed on average by 92, 88, and 76 %. Dissolved sulphates were removed in the summer up to 99%, 95%, and 67%, respectively. Alkalinity is a direct product of sulphate reduction, and its variation was found to be inversely proportional to that of sulphate removal. Unfortunately, water is also enriched with organic matter after its journey through the biofilter, with high COD, BOD, and, to some extent, phenols. The physical properties of the biofilter have been modified over time due to its compaction since its construction (6 to 10 %). Thus, the heterogeneity of the porous media has increased and preferential flow paths have been developed (shorter residence time), which could explained part of the decrease in arsenic removal in 2002. Furthermore, the geotextile near the surface of the biofilter got partly plugged by organic material limiting the infiltration. As a consequence, the maximum discharge decreased from 7 L/s in 2000 to 5 L/s in 2002. To sum up, the biofilter has improved the water quality of Wood Cadillac effluents with respect to arsenic. However, its performance has somewhat decreased in 2002 in comparison to the two previous years. This decrease is due to preferential flow paths, which shorten the residence time, and/or to less available easily degradable organic matter available to reducing sulphate bacteria. The quality of the biofilter effluent has somewhat degraded when one's consider organic matter. However, chemical and biological demands have significantly decreased in 2002 in comparison to the two previous years.

Introduction

The Wood Cadillac mine site, in North-western Quebec, features sulphide-poor, but As-rich, tailings. The mine tailings total about 210 000 m^3 and cover 21 ha, in a wedge shape body thinning from 2.5 to 0 m. The restoration focussed on the mechanical stabilization of tailings and on the treatment of As-contaminated seep and surface waters by a reducing biofilter. The As load, in these conditions, is likely precipitated as As_2S_3 (orpiment). The site characteristics and the biofilter design are described in the companion paper (Tassé *et al*., 2003).

This work reports on the biofilter performance and efficiency to treat neutral arsenic waters by sulphate reduction.

Theory

Sulphate-reducing bacteria fulfil their energy needs by reducing sulphate molecules. Sulphate reduction goes along anaerobic oxidation of organic compounds, with alkalinity production, arsenic

* submitted as a companion paper to "Wood Cadillac Mine Tailings : Design of a Biofilter for Arsenic Control" by Tassé *et al*.

precipitation as sulphides (likely orpiment As_2S_3). As a consequence, water quality, in general, is increased.

$$3SO_4^{2-} + 6CH_2O \longrightarrow 3H_2S + 6HCO_3^- \quad (1)$$
$$2As^{3+} + 3H_2S \longrightarrow As_2S_3 + 6H^+ \quad (2)$$

where CH_2O is a simple organic molecule.

pH values between 6 and 9, permanent reducing milieus, prone to react organic substrates and availability of nutriments favour the reaction (1). Bacterial catalysis is essential, since geological times are required to reduce any significant masses of sulphates at low temperatures, even as high as 100°C (Powell and Macqueen, 1984; Krouse *et al.*, 1988).

Efficiency of the biofilter

Physical and hydraulic parameters

Figure 1 shows a plan view of the biofilter with the water-sample positions: one in each of the draining canals surrounding the impoundment (stations Influent 1 and 2) and one at the outlet of the biofilter (station Effluent).

The maximum discharge rate, measured at the outlet, has decreased from 7.3 L/s in 2000 to 5.0 L/s in 2002. This decrease is due to limited infiltration and to lower conductivities related to wood-waste compaction. The feed water is not infiltrating evenly at the surface due to a partly plugged geotextile by organic matters. In fact, in some areas, the low permeability of the geotextile is so severe that methane gas, generated in the biofilter, cumulates and forms a cone with about 20 cm diameter and sufficiently high to displace 10 cm gravel layer above the geotextile before it tears it up. To solve this problem, it is suggested to remove the geotextile. Furthermore, the biofilter thickness has decreased by 6 to 10 % from 2000 to 2002, based on the elevation at four points at its surface; the reference elevation was the surface of the control chamber.

These discharge rates of 7.3 and 5.0 L/s corresponds to an equivalent homogeneous vertical-conductivities of 1E-5 m/s and 7E-6 m/s, where the maximum hydraulic gradient, 0.26, was imposed. In 2002, two piezometers (3 cm diameter, screened over 0.3 m), st-E and st-O (Fig. 1), were installed at mid-thickness of the biofilter; the horizontal-hydraulic conductivities, measured *in situ* using a constant head test, Lefranc type: CAN/BNQ 2501-135, are 2.8E-6 et 1.3E-7 m/s, indicating an heterogeneous porous media. Assuming an isotropic porous media, conductivities being equally pondered over the surface of the biofilter, and the maximum hydraulic gradient being imposed, the discharge rate can only reach 1 L/s. This value is much less then maximum discharge of 5 L/s, measured in 2002. Furthermore, since the nature of the waste creates an important anisotropy due to the preferential horizontal position of the wood-fragments, the measured conductivities are higher then the vertical one, increasing further the differences between the measured and the equivalent conductivities. Thus, in the biofilter, some zones have high conductivities allowing preferential flow paths despite wood waste compaction with time, and in these zones the residence time is, therefore, less then the 25 hrs retained for the biofilter design.

Water quality evolution

Water samples were taken at the inlets (Influents 1 and 2) and outlet of the biofilter (Effluent, Fig. 1). A duplicate was taken for quality control. Samples were measured for temperature, pH, Eh, and analysed for alkalinity (titration), sulphates (chromatography), Al, Ba, Ca, Cd, Cu, Fe_{total}, K, Mg, Mn, Mo, Na, Ni, P, Pb, Zn, and S_{total} (ICP), Arsenic (atomic adsorption), chemical oxygen demand (DCO, titrimetry), biological oxygen demand (DBO, oxygen electrode), phenols, tannins and lignins (colorimetry).

Arsenic. Figure 2 shows the evolution of the arsenic and sulphate concentrations, and their corresponding fraction removed from the feed waters, from May 2000 to October 2002. The measured discharge is also shown. The concentration of the influent corresponds to the mean concentration of Influents 1 and 2. Dissolved As was removed beyond 90 % over most of the period investigated in 2000 and 2001, even in November. Furthermore, despite feed waters with arsenic concentration of 585 µg/L (08/08/2001), its concentration in the effluent was less then 40 µg/L (93 % removal). Arsenic was likely precipitated as orpiment. The saturation indexes (MinteqA2-v4) indicate saturation with respect to orpiment for the water quality at the effluent. The lowest

performance is observed in spring 2000 (60 % removal); this is likely due to the time required for the bacteria flora to establish; furthermore, spring waters are cold, which limits bacterial activity. Despite this low activity, the As concentration in the effluent was maintained below 25 µg/L since arsenic in feed-water is low in the spring due to dilution related to snow melt. In August 2002, the As concentrations decrease from 250 µg/L to 50 µg/L or 80 % removal. This lower removal fraction in comparison to those observed for the same period in 2000 and 2001 is likely due to preferential flow paths in the biofilter, which reduce the residence time, and/or to less available easily degradable organic matter available to reducing sulphate bacteria.

Sulphates. The characteristic H_2S smell of reduced sulphur was noted in the control chamber, which is clear evidence that sulphate reduction is going on (Eq. 1). Since bacterial activity is higher at warmer temperature, it is in the summer that dissolved sulphates are most removed from the feed-waters, up to 99%, 95%, and 67% in 2000, 2001, and 2002. The negative values observed in fall 2000 might be due to sulphide oxidation occurring in the biofilter by dissolved oxygen. In fact, the potential redox in the effluent had rose to –111 mVolts in 11/14/2000 from –287 mVolts in 10/31/2000. Cold temperatures may also have limited organic oxidation, but not the sulphide one. Plus, the residence time was the shortest as maximum discharge rate occurred. Similar behaviour was also observed in fall 2002.

pH. Figure 3 shows that pH of the effluent is always below that of feed water due to the presence of organic acids and to some degree the H^+ generated by sulphides precipitation (Eq. 2). This gap shrinks with time mainly as the easily leachable organic acids decrease and as the alteration profiles in the impoundment get stabilized.

Alkalinity. Alkalinity is a direct product of sulphate reduction (Eq. 1) and is reflected by the high correlation coefficient, 0.95, between the moles of sulphates removed to those gained in alkalinity (Fig. 4). Thus, sulphide precipitation and acid generation (Eq. 2) is limited as metal concentrations of the feed waters are low. Carbonate precipitation is also small, as the calcium concentration remains essentially unchanged as the water migrates through the biofilter (Fig. 3). Furthermore, the saturation indices show an undersaturation with respect to calcite and aragonite for the water quality at the effluent. For the range of pH observed in 2002, between 6.3 and 6.9, the alkalinity of the effluent is mainly one of bicarbonate (HCO_3^-).

Iron. Total dissolved iron concentration is low in the feed water, <2 mg/L (not shown). However, its concentration has increased slightly as the water migrates through the biofilter in 2000, while it was, in general, the opposite in 2001, and it remains essentially unchanged in 2002 at <0.3 mg/L-Fe_{total}. These low concentrations in 2002 indicate the stabilisation of the alteration profiles in the impoundment. In 2000, fine particles containing some iron oxy-hydroxides entered in the biofilter and/or were trapped with the organic wastes, and got reduced within the biofilter. Consequently, the dissolved iron had increased in the effluent. In 2001, Fe^{2+} decreased since it was precipitated as pyrite and/or siderite in the biofilter.

Nickel. Ni concentration in the feed water is low, <0.2 mg/L (not shown); it gets precipitated out likely as sulphides in the biofilter, and its concentration in the effluent is maintained below the detection level, which is 0.02 mg/L in 2000-01, and 0.03 mg/L in 2002.

Manganese and Barium. The manganese concentration, as for iron, is not very soluble in its oxidized state (Mn^{3+}) and soluble in its reduced state (Mn^{2+}). Both, manganese and barium, follow the same pattern. Manganese oxides, and manganese and barium sulphates can be present in suspended particles in the feed waters and/or with the organic wastes of the biofilter. The reducing environment favours their reduction and the metal solubilisation, as a consequence higher metal concentrations are observed in the effluent in comparison to that in the influent (Fig. 3 shows only Mn_{total} evolution). With time, the impoundment profiles got stabilized and their maximum concentrations in the effluent were 1.2 mg/L-Mn_{total} and 0.5 mg/L-Ba, in 2002, in comparison to 7 and 1.3 mg/L in 2000.

Cadmium, chrome, cupper, lead, molybdenum, and zinc. Either in the influent or effluent, these metal concentrations are at all time at or near the detection limits, which vary between 0.015 and 0.003 mg/L.

Organic parameters. The reducing environment is reflected by the high chemical oxygen (COD, Fig. 3) and biological demands (BOD, not shown). These demands decrease over the years as the easily leachable organic compounds have been leached out. But, the maximum phenols concentration decreases only slightly over the three years of investigation (Fig. 3). Nevertheless, this is believed to be a temporary situation. Other large wood waste deposits show that the pore water improves relative to phenols with time. Nonetheless, easily degradable organics will remain available over long period of times as long as the biotransformation of the organic matters will take place. For example, the lignin Syringyl (type of polyphenols) plays an essential role in the biotransformation of organic matter, as well as other numerous polyphenolic compounds (Stevanovic-Janezic, 1998).

Conclusions

At the Wood Cadillac site, the reductive biofilter treats efficiently the arsenic-rich effluent, where arsenic is precipitated as a sulphide (likely As_2S_3). Relative to mean input concentration of 103, 227, and 168 µg/L-As in 2000, 2001, and 2002, arsenic was removed on average by 92, 88, and 76 %, respectively. At the outlet, dissolved arsenic was maintained below 57 µg/L during the entire period investigated, except June 20th 2001 (93 µg/L). Up to 99%, 95%, and 67% of the dissolved sulphates were removed in the summer of 2000, 2001, and 2002. Alkalinity is a direct product of sulphate reduction, and its variation was found to be inversely proportional to that of sulphate removal. Unfortunately, water is also enriched with organic matter as the water flows through the biofilter, with high chemical and biological oxygen demands in the first two years of operation. In 2002, a significant decrease is observed for these demands; phenols have also decreased, but less significantly than DCO and DBO did.

The geotextile near the surface of the biofilter got partly plugged by organic material limiting the infiltration. Furthermore, the compaction of the biofilter has increased the heterogeneity of the organic layer since its construction. As a consequence, the maximum discharge rate decreased from 7 to 5 L/s between 2000 and 2002.

In brief, the water quality of Wood Cadillac effluents has improved significantly with respect to arsenic. However, that quality has somewhat degraded when one's consider organic matter. However, chemical and biological demands have significantly decreased in 2002 in comparison to the two previous years.

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Acknowledgments

This work was carried out with the financial help of Natural Resources - Québec.

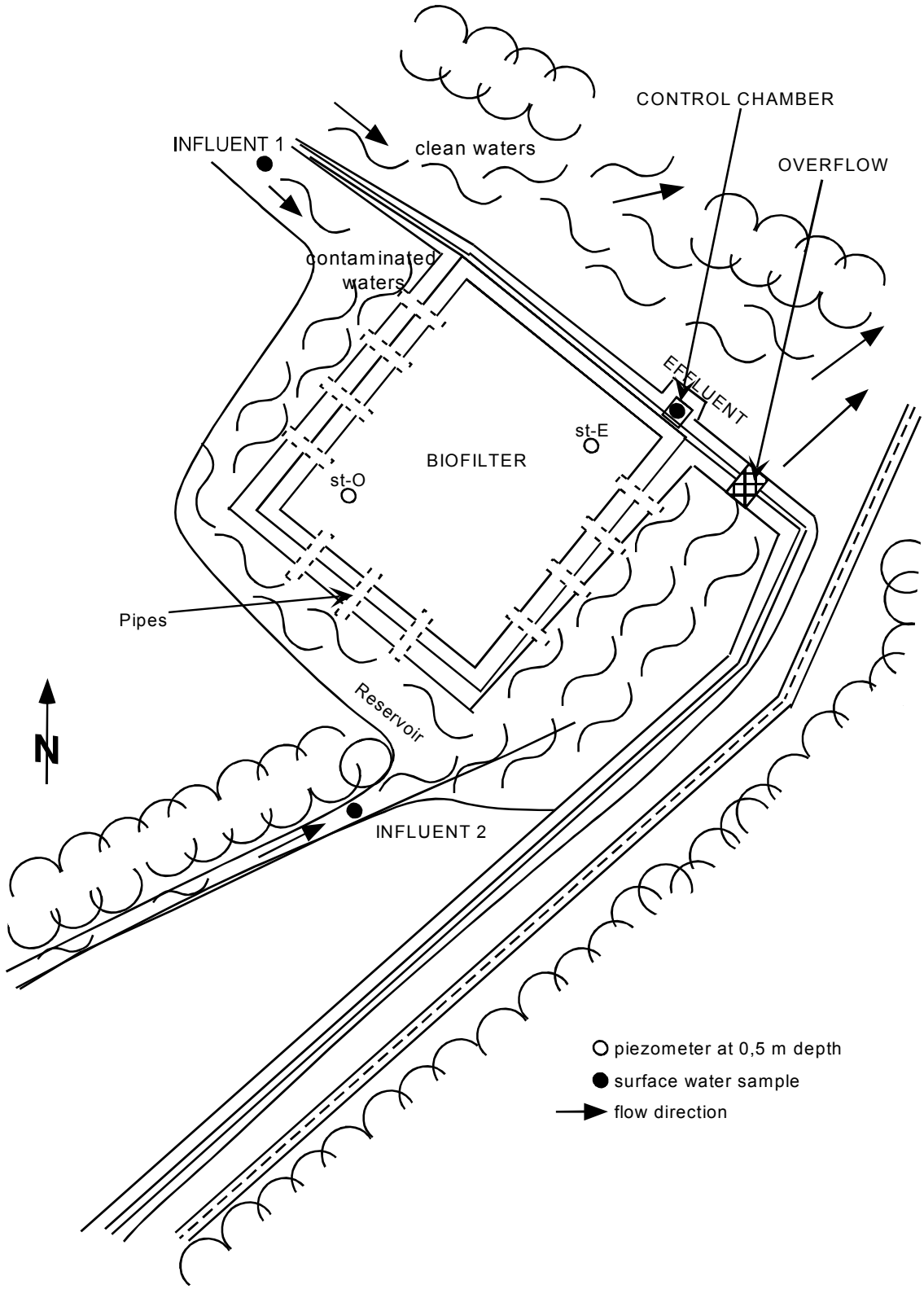

Figure 1. Schematic plan view of the water treatment system at the Wood Cadillac mine site.

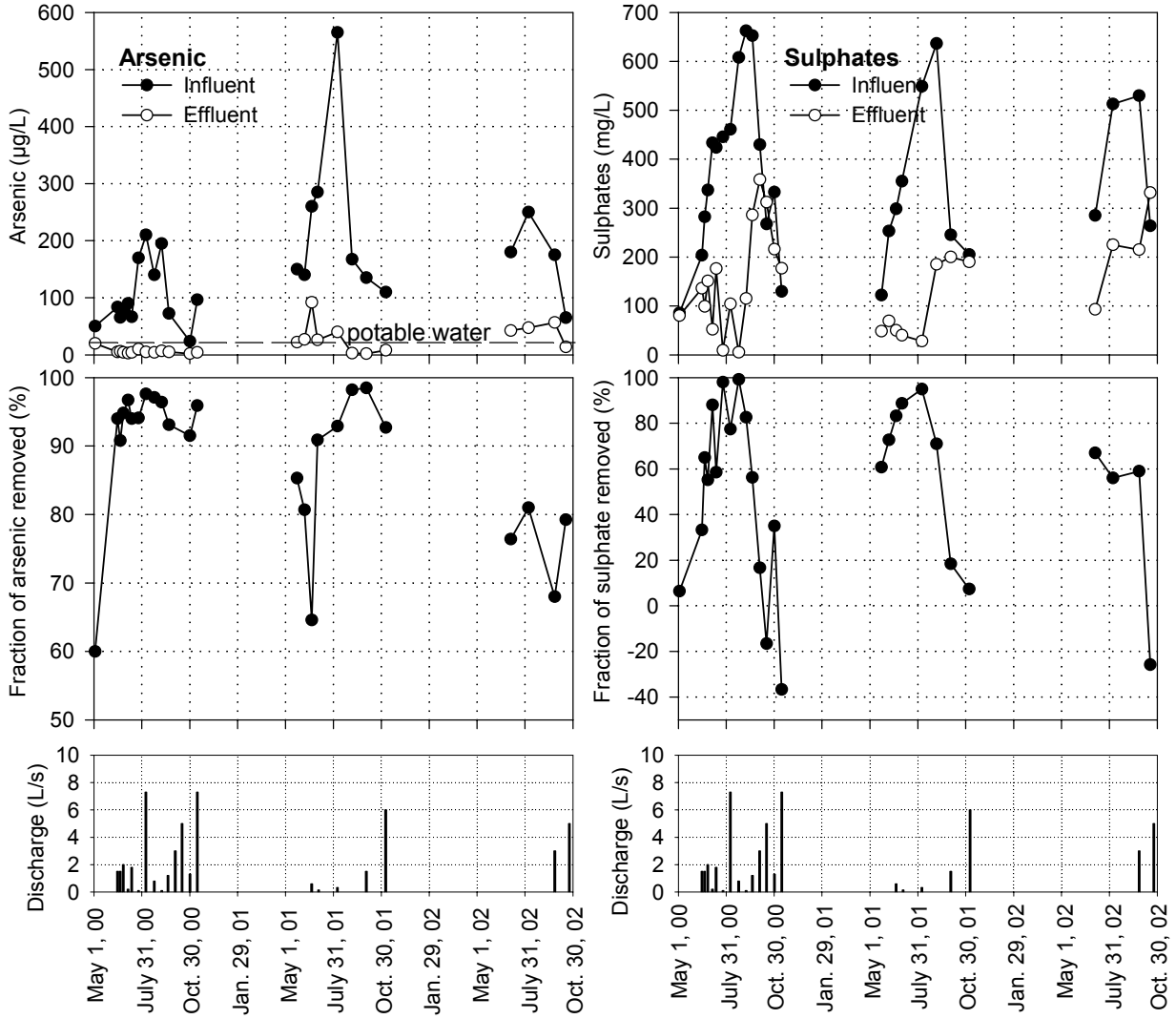

Figure 2. Arsenic and sulphates at the influent and effluent of the biofilter, and their respective fraction removed from May 2000 to October 2002. Measured discharge rates are also shown.

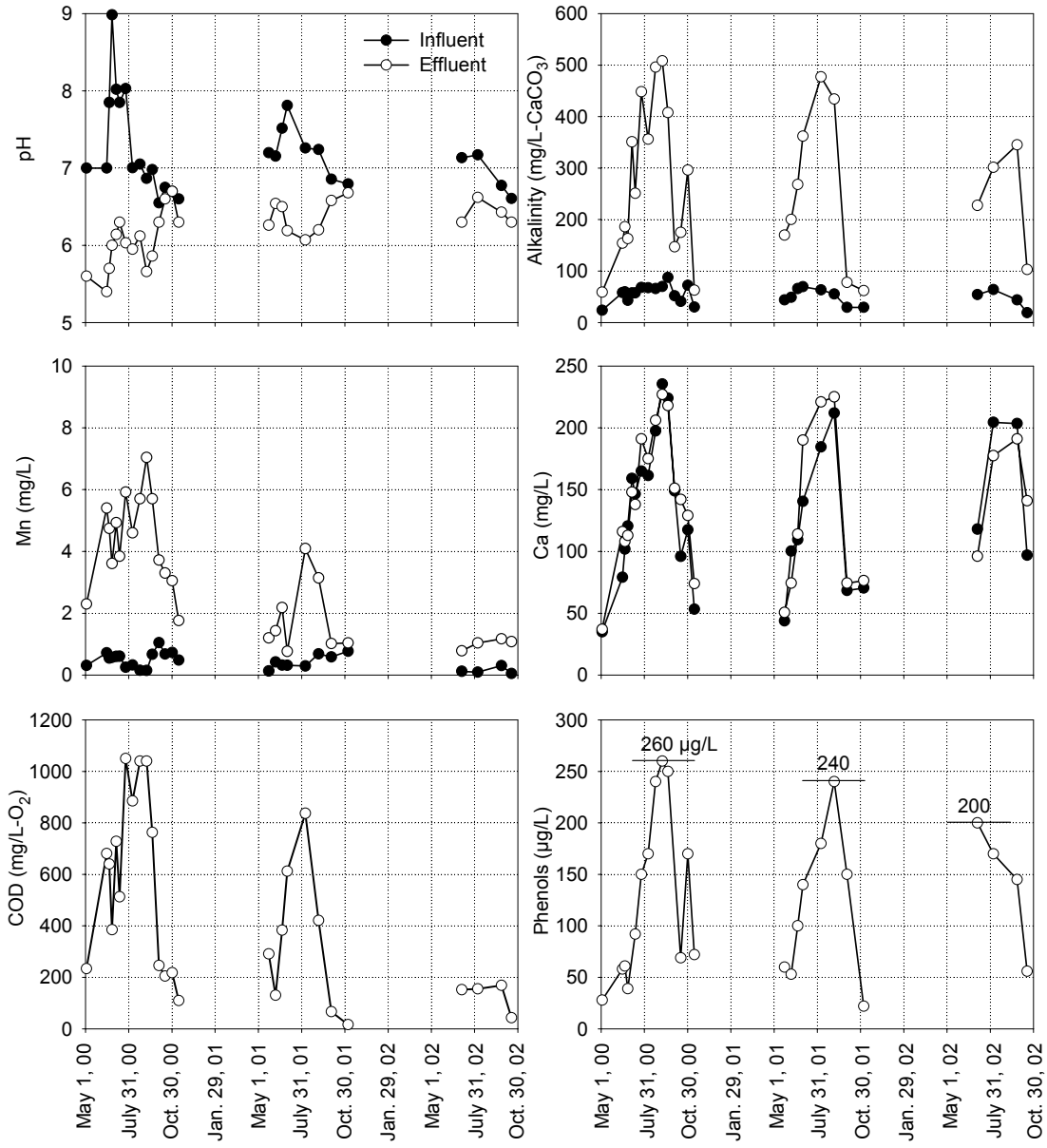

Figure 3. Evolution of the water quality with respect to pH, alkalinity, nickel, manganese, chemical oxygen demand (COD), and phenols: May 2000 to October 2002.

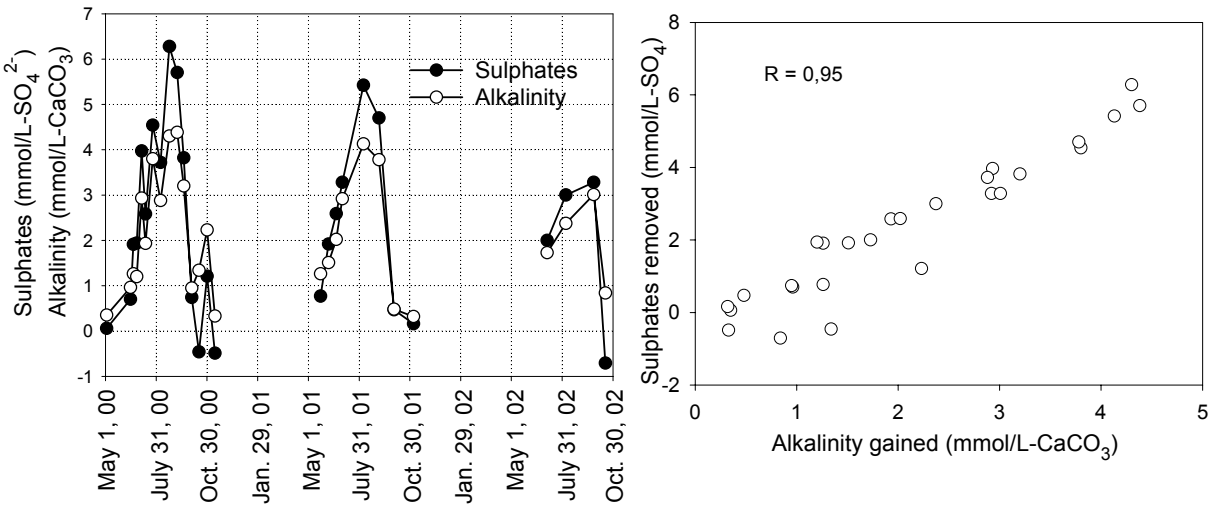

Figure 4. Alkalinity gained and sulphates removed from May 2000 to October 2002.