

Elucidation of the factors controlling the oxidation kinetics of manganese in passive treatment systems : monitoring of aerobic wetland removal technologies

Charlotte Lafont^{1,2}, Éric D. van Hullebusch¹, Fabienne Battaglia-Brunet², Stéphane Vaxelaire²

¹Université Paris Cité, Institut de Physique du Globe de Paris, CNRS, 75005, Paris, France, lafont@ipgp.fr

²Bureau de Recherches Géologiques et Minières, 45060 Orléans, France

Abstract

The determination of parameters controlling the oxidation kinetics of manganese (Mn) during passive treatment is essential to improve the management of mine drainage water treatment. Mn removal processes are mainly driven by microorganisms, but the conditions controlling Mn removal efficiency have not been elucidated yet. To distinguish the factors associated with Mn removal efficiency, the surface water of a passive treatment plant composed of Phragmite-wetlands was monitored for one year. It has been observed that the Mn removal efficiency vary with the concentration of suspended iron particles and the water temperature.

Keywords: Manganese, iron, removal efficiency, neutral coal mine drainage water, wetland

Introduction

France, like many other countries, faces environmental and long-term management challenges caused by mine drainage waters as a result of historical coal mining activities. Thus, passive water treatment plants have been designed to remove manganese (Mn) from mine drainage water before discharge into natural water bodies (Neculita and Rosa 2019). A treatment plant composed of constructed aerobic wetlands systems, located in Alès (South-East France), aims to remove Mn and iron (Fe) from a neutral coal mine drainage water. In these systems, dissolved Mn is oxidised and precipitates as Mn(III/IV) minerals. During passive treatment of neutral mine drainage water, it is now well established that the processes governing Mn oxidation are mainly controlled by biological processes and autocatalytic mechanisms (Skousen *et al.* 2017). Previous studies have highlighted the difficulties to remove Mn during passive treatment (Watzlaf *et al.* 2004). Indeed, Mn removal efficiency is highly variable, depending on mine drainage water chemistry and passive treatment configuration (Hallberg and Johnson 2005; Batty *et al.* 2005; Bamforth *et al.* 2006; Tan *et al.* 2010; Le Bourre *et al.* 2020; Jacob *et al.* 2022). In this context, the present study aims to specify

the factors influencing Mn oxidation kinetics by a one-year monitoring programme of the temporal evolution of geochemical and physical-chemical parameters at a coal-mine water treatment plant.

Methods

The studied passive water treatment plant is located in Alès (South-East France). It is composed of aerobics wetlands for Mn and Fe removal. It includes a six-step oxygenation cascade, a settling pond of 2400 m² with a depth of 6 m and three *Phragmite*-planted wetlands of 1540 m², 1480 m² and 1750 m², respectively (Fig. 1). Mine drainage water is pumped from the old coal mining galleries and injected at the inlet of the water treatment plant at an average flow rate of 105.9 ± 3.3 m³.h⁻¹. The mine drainage water is mainly composed of sulphate, carbonate and of Fe and Mn which are the targets contaminants.

From march 2022 to February 2023, surface waters of the passive treatment plant were sampled and analysed for their chemical composition every two months. In order to determine the Mn and Fe removal efficiency of process unit, water samples were collected at different points through the treatment plant (Fig. 1). Sampling was carried out from the less contaminated point to the most

contaminated point (i.e. from the station outlet to the station inlet). Filtered (0.45 µm, cellulose acetate filters, Sartorius) and unfiltered fraction of the surface water was sampled for each point. Vacuum-filtration was done onsite with a Nalgene filtration unit. For dissolved and total major ions analysis, aliquots of filtered and non-filtered water were acidified with nitric acid (HNO₃ 0.1 M). For Fe(II) measurement, an aliquot of filter water was acidified with concentrated hydrochloric acid (HCl) (Kirby *et al.* 1999). Unfiltered water was kept for the titration of alkalinity. Filtration blanks were done onsite with MilliQ water for each measured parameter. Samples were stored at 4°C until analysis. The physicochemical parameters (temperature (T), pH, redox potential (ORP), dissolved O₂ (DO) and electrical conductivity (EC)) of all sampled waters were measured onsite with field WTW® 3430.

Bulk concentrations of dissolved and total major elements (Ca, Mg, Na, K, Mn, Fe, Al, P and Zn) of sampled surface water were determined by ICP-OES (SPECTROGREEN, SPECTRO Analytical Instruments). Quality control solution containing multi-element were used to assess accuracy and reproducibility of the analytical method. Dissolved Fe(II) concentrations were measured by 1,10-phenanthroline method described by Kirby *et al.* (1999). Alkalinity measurements were performed using HCl 0.1 M titration according to the standard Gran method (Gran 1952). Removal efficiency

calculation was done using Eq. 1. Total Mn concentration at the inlet and at the outlet of the passive treatment plant was considered to calculate the total removal efficiency of the treatment plant.

$$Mn \text{ removal efficiency (\%)} = \frac{([Mn]_{inlet} - [Mn]_{outlet})}{[Mn]_{inlet}} \times 100 \quad (Eq. 1)$$

A principal component analysis (PCA) was performed to highlight the factors involved in Mn removal efficiency. Data from all the sampling campaigns were used. Physicochemical parameters and water composition (i.e. T, pH, ORP, DO, EC, dissolved Mn, dissolved Fe, total Fe concentrations and alkalinity) were selected to carry out PCA. Total major ions results from some sampling points (Wetland 1 in June 2022 and Wetland 2 in April and June 2022) have been excluded due to an overestimation of the concentration caused by resuspension of sediment during sampling. This analysis was performed by R software using the FactoMineR package.

Results

Physicochemical parameters (T, pH, ORP, DO and EC) were measured at each sampling point and at every sampling campaign. At the pumping sample point (inlet, Fig. 1), the water showed a stable pH around 6.5, dissolved O₂ at 0 mg.L⁻¹, redox potential values between -35.4 mV and -67.8 mV and temperature values between 22.2 °C to 24.6

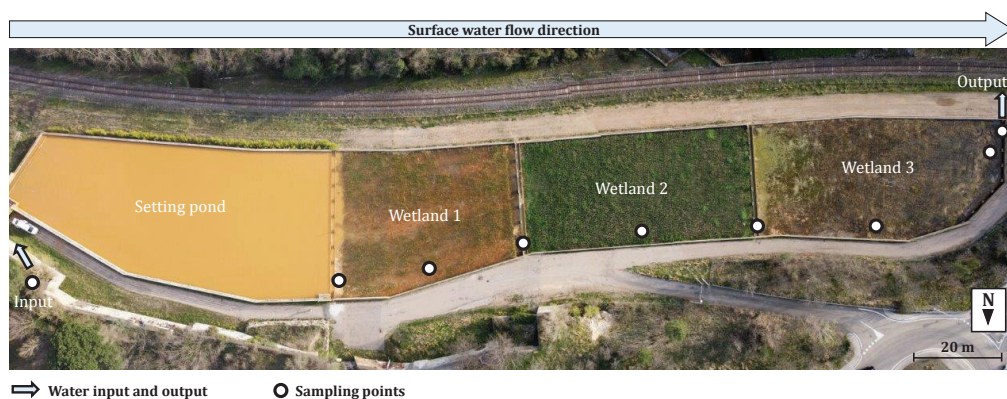


Figure 1 Sampling locations in the studied passive treatment plant, Wetlands 1, 2 and 3 are composed of Phragmite plants (image: F. Duré, BRGM).

°C. Along the passive treatment plant, these parameters increased up to a pH around 8 and positive values of O_2 and ORP were found. In the wetlands, the water temperature was found to vary with the seasons. The highest temperatures were recorded in June and August, with an average value of 25 °C. The lowest temperatures were recorded in December, with a value of 15 °C. It should be taken into account that the measured surface water temperatures depend on the sampling time, which is not representative of the temperature evolution during the day.

Mn and Fe concentrations decrease in surface water during the treatment process (Fig. 2, D). These concentrations have been shown to vary with sampling campaigns season time. Significant decreases in Mn concentration across all wetlands are observed in April, June and February. In August, October and December, Mn only shows a significant decrease of its concentration in the last wetland (Wetland 3 and End Wetland 3, see Fig. 2, D). Mn removal efficiency was calculated considering Mn inlet and outlet concentrations (Eq. 1). As shown in Figure 2, the highest Mn removal efficiency was around 92% in June and at its lowest value (43%) in December. Fe was characterized by

its dissolved and total content. At all sampling campaigns, dissolved Fe concentrations are significantly low after passing through the settling pond, generally found under 0.2 mg.L^{-1} (Fig. 2, A and B). In contrast, total Fe concentrations are gradually decreasing through the wetlands (Fig. 2, C). It decreases with average concentrations going to $9.43 \pm 3.37 \text{ mg.L}^{-1}$ to $0.57 \pm 0.62 \text{ mg.L}^{-1}$. In wetlands, because dissolved Fe concentrations are significantly low, total Fe can be considered as Fe particles larger than $0.45 \mu\text{m}$. For this parameter, missing data occurs due to concentration overestimation caused by sediment remobilisation during sampling.

PCA results, presented in Fig. 3, show 74.67% of the total inertia of the dataset, allowing to observe most of the variability of it (i.e. 60.66% for dimension 1 and 14.01% for dimension 2). The graph of variables can be divided into four main clusters (Fig. 3, A). Cluster 1 is composed of DO, pH and ORP. The second includes Fe and total Fe concentrations. The third one is associated with alkalinity and Mn concentration. Cluster 4 is represented by EC and temperature. Figure 3 allows to observe correlated and anticorrelated parameters during passive treatment of mine drainage water. The first

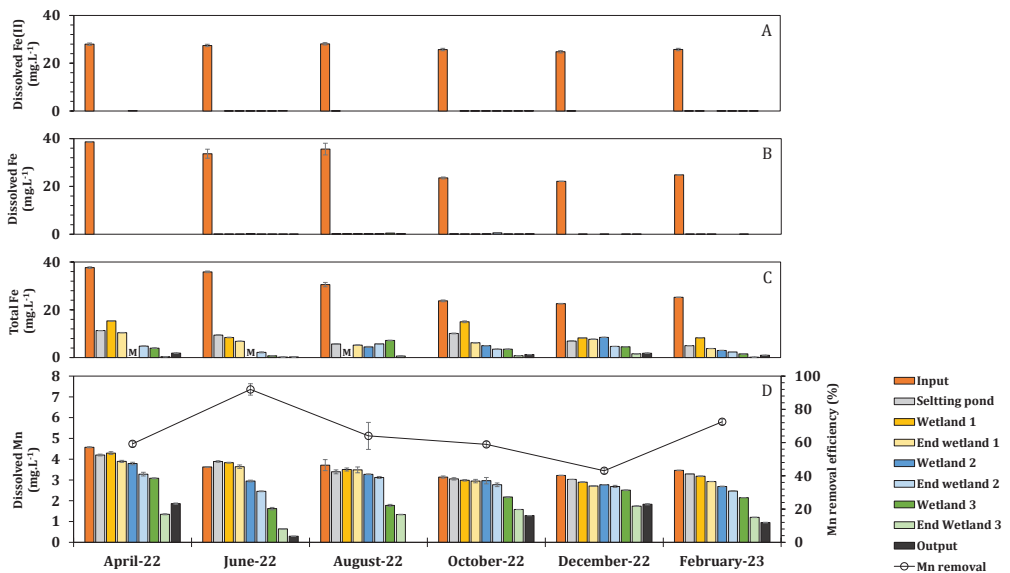


Figure 2 Evolution of (A) dissolved Fe(II), (B) dissolved Fe, (C) total Fe and (D) dissolved Mn concentrations in surface mine water through the studied passive treatment plant (M refers to missing data).

interesting observation is the anticorrelation of Fe, Total Fe, alkalinity, Mn, Temperature and EC parameters compared to the pH, DO (25°C) and ORP parameters according to dimension 1. It represents the differences comparing physicochemical characteristics of inlet water and the outlet treated water, which is illustrated by sampling points qualitative variables (Fig. 3, B). The sampling dates, added as a qualitative supplementary variable (Fig. 3, B), expose the seasonal effects on water physiochemistry. It shows similarities in water chemistry when comparing sampling time. Two main groups are distinguished, on one hand, the sampling campaigns of April 2022, June 2022 and August 2022 and on the other hand the sampling campaigns of October 2022, December 2022 and February 2023.

Discussion

The design of aerobic wetland for passive water treatment is largely dependent on the mine drainage pH and on the concentration of contaminants which is affected by the geology of the mine site. It is especially valid for Mn removal which is particularly dependent on Fe water content (Calugaru *et al.* 2021). Furthermore, the poor understanding of the mechanisms and factors controlling manganese removal is an obstacle to define design criteria for treatment plants (Neculita and Rosa 2019). Therefore, Mn removal effectiveness can be highly variable comparing treatment plants (Hallberg and Johnson 2005; Lesley *et al.* 2008; Tan *et al.* 2010; Jacob *et al.* 2022). The

discussion below relates some parameters impacting the elimination of Mn in a passive water treatment plant to better understand variations in Mn removal efficiency.

The water DO, pH and ORP increase all along the plant, creating optimal conditions for Fe oxidation. For Mn abiotic oxidation optimal parameters are not reached during passive treatment process. In this kind of systems, biotic oxidation processes most likely control Mn oxidation. But in these environments, the optimal conditions for biotic Mn removal remain unknown. Our results show that manganese removal efficiency decreases with temperature, from high temperature conditions in June to lower temperature conditions in December (Fig. 2). The biological oxidising activity of Mn is probably controlled by temperature seasonal variations. Previous studies have shown that some microorganisms were able to oxidise Mn at temperatures similar to those recorded in June (Neculita and Rosa 2019). Recent studies, carried out in laboratories, have observed Mn oxidation processes by microorganisms at different temperatures. Yu and Leadbetter (2020) observed an optimal Mn oxidation at temperatures ranging between 34 °C and 40 °C. This result was in line with those reported by Boogerd and de Vrind (1987), who have studied especially manganese oxidation by *Leptothrix discophora*. But as described by Neculita and Rosa (2019), several laboratories experiments have observed microbial communities that can efficiently contribute to Mn oxidation at temperature as low as 4°C. Studies of real

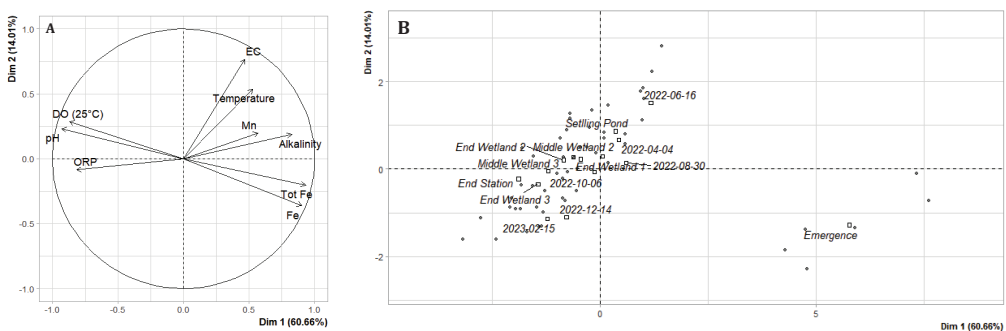


Figure 3 Principal Component Analyses (PCA) based on water physicochemical variables (pH, T, EC, ORP and DO corrected at 25 °C, dissolved Mn (Mn), dissolved Fe (Fe), total Fe (Tot Fe) concentrations and alkalinity), (A) Graphic of variables and (B) Graphic of individuals.

constructed wetland for coal mine drainage water treatment have also brought diverse conclusions on temperature effect but have also consider other factors to explain removal variation such as pH, DO, alkalinity, nutrient availability (Ye *et al.* 2001). Temperature appears to be a key parameter affecting Mn removal efficiency by biotic process, indeed the activity and development of certain Mn-oxidising microbial communities seems temperature dependant.

The simultaneous presence of Fe and Mn in mine drainage water has already been reported as a limiting parameter for Mn removal during passive water treatment (Lesley *et al.* 2008). Indeed, it is well known that ferrous iron can reduce Mn oxidised forms (Liu *et al.* 2022). Our results shows that dissolved Fe and dissolved Fe(II) concentrations are close or under the limit of analytical detection at wetlands sampling points (Fig. 2). In contrast, total Fe considering as Fe particles larger than 0.45 μm , is found at different concentrations through the wetlands. Due to water pH, ORP and dissolved organic carbon concentrations (i.e. $< 1 \text{ mg.L}^{-1}$), we hypothesize that total Fe can be defined as Fe oxide(hydroxides) aggregate in water suspensions. Figure 4 was plot to study the impact of total Fe concentration on Mn removal. This graph shows the evolution of the Mn concentration as a function of the total Fe concentration along the station and for different sampling campaigns. Our results shows that Mn concentrations significantly decrease when total Fe concentration is below

5 mg.L^{-1} in surface water. Watzlaf *et al.* (2004), who have studied a real passive treatment plant, reported that most of Mn removal takes place in "iron-free zone" corresponding to surface water containing low suspended Fe particles. Our results are consistent with Watzlaf *et al.* (2004) observations, significant Mn removal were found in wetland 3 which contained the lowest total iron concentration. However, these observations require further investigation to understand the interdependence of Fe and Mn biogeochemical cycling in this environment.

Conclusions

This study presents data from a one-year monitoring programme of a coal-mine water treatment plant in order to highlights which factors affect the Mn removal efficiency. According to the results, Mn concentrations are dependent to water temperature and suspended Fe particles concentrations. Indeed, the higher Mn removal efficiency was observed during summer season when total Fe removal efficiency was the highest. We hypothesised that the microbial communities that oxidise Mn in this environment are temperature dependent. Also, it appears that Fe particles larger than 0.45 μm have an impact on Mn oxidation, but this needs to be understand by further investigations. It would be interesting to determine whether if the presence of suspended Fe in mine water has an impact on Mn biotic oxidation to predict long-term Mn immobilization in passive water treatment plants.

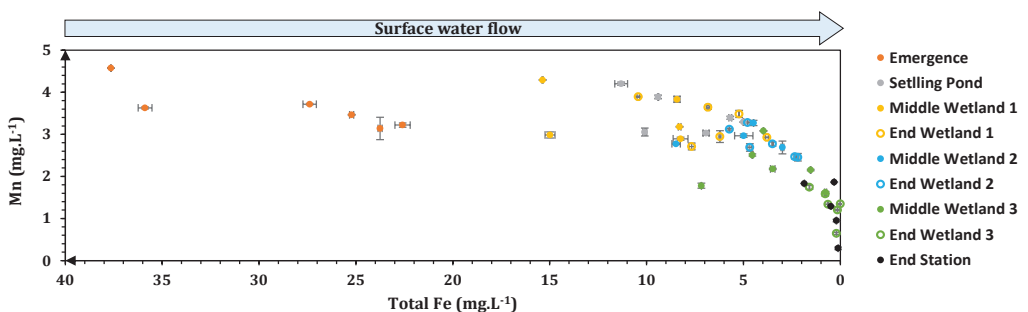


Figure 4 Dissolved manganese and total iron (fraction $> 0.45 \mu\text{m}$) in surface waters sampled through the passive treatment plant. Sampling locations are illustrated Fig. 1.

Acknowledgements

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