Antimony Passive Treatment by Two Methods: Sulfate Reduction and Adsorption onto AMD Precipitate

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ABSTRACT

Two different passive water treatment methods to remove antimony from mine water were tested in field trials at a gold mine in New Zealand. In one method, antimony was removed through adsorption onto iron oxyhydroxides. The oxyhydroxides were collected from precipitate within an acid mine drainage discharge at a nearby coal mine. In the other treatment method, antimony was removed through precipitation as antimony sulfide (stibnite) in a sulfate-reducing bioreactor. Each system consisted of a 1000 liter plastic tub, filled with the treatment media. The loading ratio of iron oxyhydroxide in the adsorption chamber was 253 grams of precipitate per liter of water. The bioreactor contained equal parts of post peel, bark and compost. Inlet antimony concentrations ranged from 0.3 to 2.3 mg/L. Hydraulic residence times ranged from three minutes to 14 hours (adsorption chamber) and two hours to 30 hours (bioreactor). Removal rates in the adsorption chamber were 14 % at residence times of only three minutes and were up to 95 % at residence times greater than 2.5 hours. As the experiment progressed, removal rates by the adsorption chamber decreased over time, suggesting that adsorption capacity was being approached. Removal rates in the bioreactor were greater than 80 % at residence times above 15 hours. The greatest removal rate was 98 % at a residence time of 30 hours. Quantitative analysis using a scanning electron microscope confirmed the presence of stibnite in the bioreactor. Bioreactor performance continued to improve over time when compared to the adsorption chamber. This difference is possibly due to multiplication of sulfate-reducing bacteria. These results show that passive treatment can be a successful treatment method for antimony at gold mine sites, and that treatment through sulfate reduction and precipitation as stibnite is a favorable long-term treatment method over a treatment method using adsorption onto iron oxyhydroxides.

Keywords: Antimony, Passive Treatment, Adsorption, Sulfides

INTRODUCTION

The metalloid antimony (Sb) is often associated with gold mines, typically in the form of the sulfide mineral stibnite (Sb_2S_3) (Nesbitt et al., 1989; Williams-Jones & Normand, 1997). Removal techniques for Sb from solution are similar to those for arsenic (As) and include coagulation with ferric chloride, ion exchange, membrane filtration, and adsorption onto ferric hydroxide (Kang, 2003; Cumming et al., 2007; Klimko et al., 2008; Nokes, 2008). Other workers have documented potential removal of Sb through sulfate reduction and formation of stibnite. Biswas et al. (2009) conducted an experiment in a test tube to show that Sb can be removed as a sulfide in the presence of sodium sulfate. Wilson & Webster-Brown (2009) suspected that precipitation of stibnite could be occurring naturally at the bottom of Lake Ohakuri along the Waikato River where concentrations of hydrogen sulfide and Sb approach stibnite saturation conditions.

Trumm & Rait (2011) conducted a laboratory column leaching experiment to test removal of Sb from mine water in New Zealand by two different passive treatment methods. In one method, Sb was removed through adsorption onto iron oxyhydroxides. The oxyhydroxides were collected at two different coal mines where precipitate was forming within acid mine drainage (AMD). In the other treatment method, Sb was by removed through sulfate reduction and precipitation as stibnite in a sulfate-reducing bioreactor. Both techniques were effective in reducing the concentration of Sb in the mine water and X-ray powder diffraction analysis of the bioreactor substrate showed that stibnite had formed.

In this work, we extend the results of Trumm & Rait (2011) by installing small-scale passive treatment systems at the OceanaGold Globe Progress Gold Mine near Reefton on the West Coast of New Zealand to field test removal of Sb by two different techniques:

- Adsorption onto AMD precipitates in an adsorption reaction chamber
- Precipitation and formation of stibnite in a sulfate-reducing bioreactor

METHODS

Two passive treatment systems were constructed using 1000 L plastic tubs (standard intermediate bulk containers) with PVC piping, alkathene piping, and associated valves. The adsorption chamber was filled with a mixture of gravel and AMD precipitate from a nearby abandoned coal mine, composed primarily of goethite and ferrihydrite (Rait et al., 2010). The loading ratio of iron oxide in the adsorption chamber was 253 g precipitate per liter of water. The bioreactor was filled with equal proportions of post peel, bark chips, and compost. Each system was constructed in an up-flow configuration, such that the inlet was at the base of each system and the water flowed upwards through the treatment media driven by sufficient hydraulic head (Figures 1 and 2).

The systems operated for a period of 71 d. Flow rates were varied to determine Sb removal for different hydraulic residence times (HRTs). Inlet and outlet samples were collected approximately three times per week from each system, or more often for very short HRTs, and analyzed for dissolved As, dissolved Sb, and sulfate by inductively coupled plasma mass spectrometry using APHA method 3125-B (for metalloids) and by ion chromatography using APHA method 4500-PG (for sulfate) (APHA, 2005). Solid samples were collected from the top 10 cm of the bioreactor for mineralogical analysis by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDS) and also for microbiological analysis.

Figure 1 Adsorption chamber prior to being filled with treatment medium

Figure 2 Adsorption chamber (on left) and bioreactor (on right) prior to being filled with water

RESULTS AND DISCUSSION

Adsorption chamber

Inlet concentrations to the adsorption chamber ranged from 0.3 to 2.3 mg/L. The system removed as much as 95 % of the inlet Sb concentrations (to as low as 0.09 mg/L) (Figure 3). The greatest percentage removal was noted at the beginning of the experiment, with removal effectiveness decreasing over time. A drop in treatment effectiveness with time likely indicates that adsorption capacity of the treatment media was being approached. Since HRT varied, it is possible to analyze the effectiveness of similar HRTs over the duration of the experiment. In general, the effectiveness of each HRT dropped with time (Figure 4). This suggests that if a consistent removal rate is required, HRT must be increased over time.

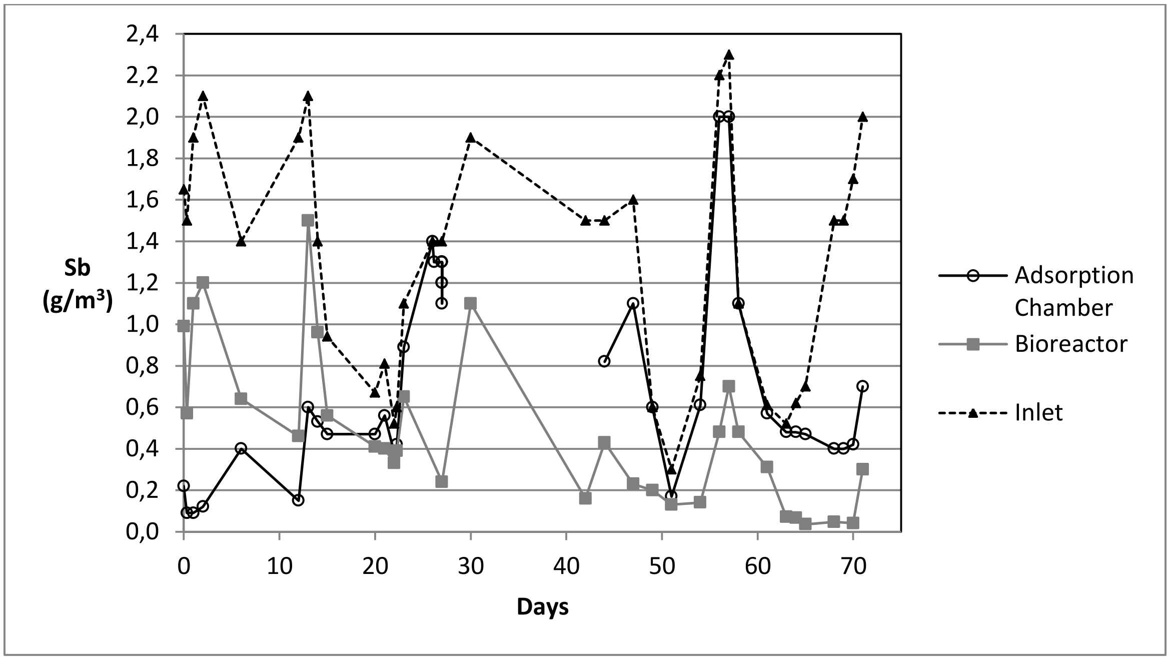

Figure 3 Inlet and outlet Sb concentrations for adsorption chamber and bioreactor over the duration of the field trials

At the very short HRT of 3 min, Sb removal in the adsorption chamber was 14 %, lowering Sb concentrations from 1.4 to 1.2 mg/L (Figure 5). Removal increased to 95 % at an HRT of 2.4 h (lowering Sb concentrations from 1.9 to 0.09 mg/L). For HRTs longer than 10 h, however, Sb removal was only 65 to 75 %. This is likely because Sb removal at these low flow rates were tested at the end of the experiment, after much of the adsorption capacity of the material had been exhausted and removal efficiency had declined.

Bioreactor

Antimony removal in the bioreactor was as low as 29 % near the beginning of the experiment, increasing to 98 % at the end of the experiment (Figure 6). Unlike the adsorption process where removal was initially good and decreased with time, Sb removal in the bioreactor was lower initially and improved with time, possibly due to growth and establishment of the sulfate-reducing bacteria population.

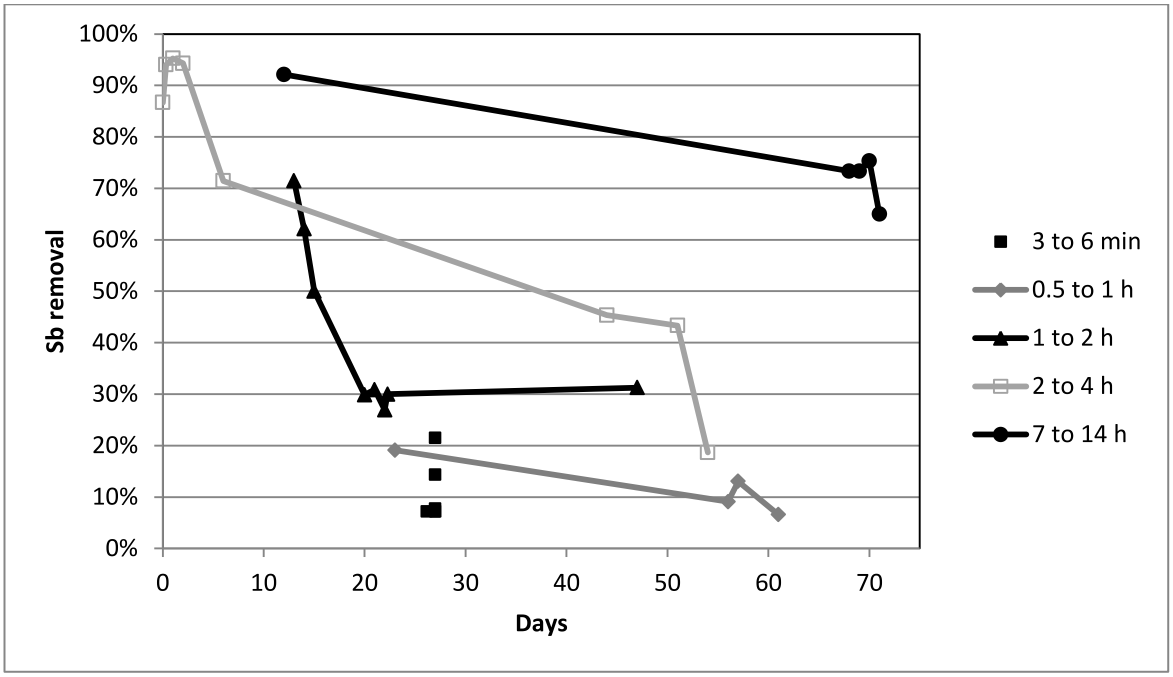

Figure 4 Antimony removal by adsorption chamber grouped according to HRT in the system to show trends

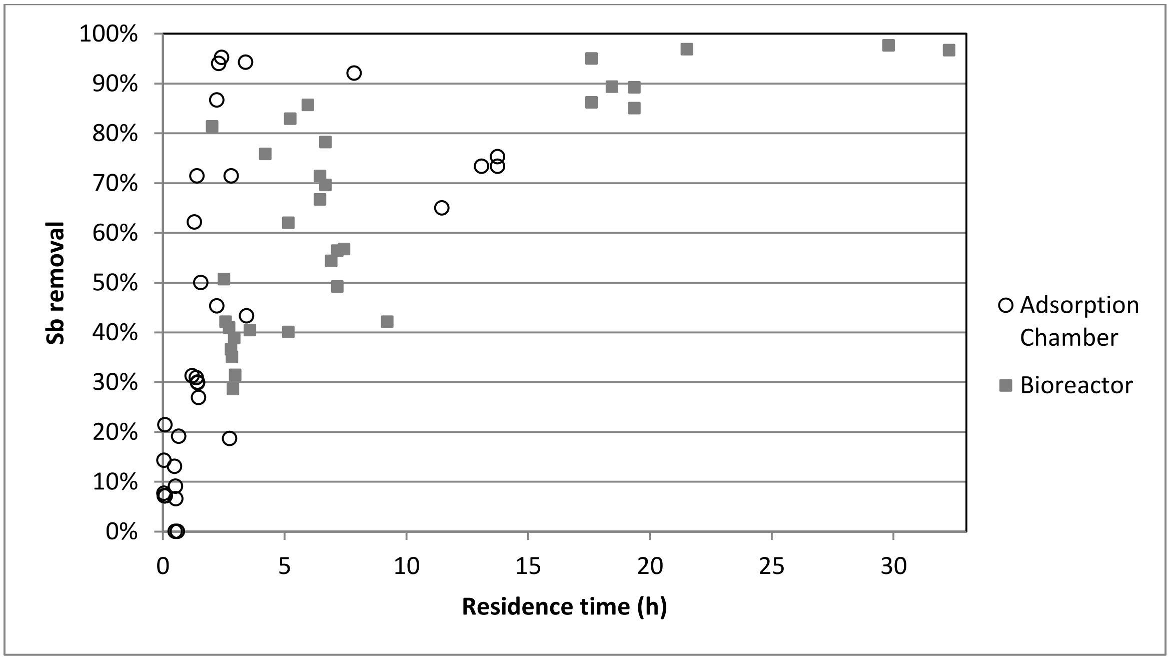

Figure 5 Antimony removal by adsorption chamber and bioreactor according to HRT

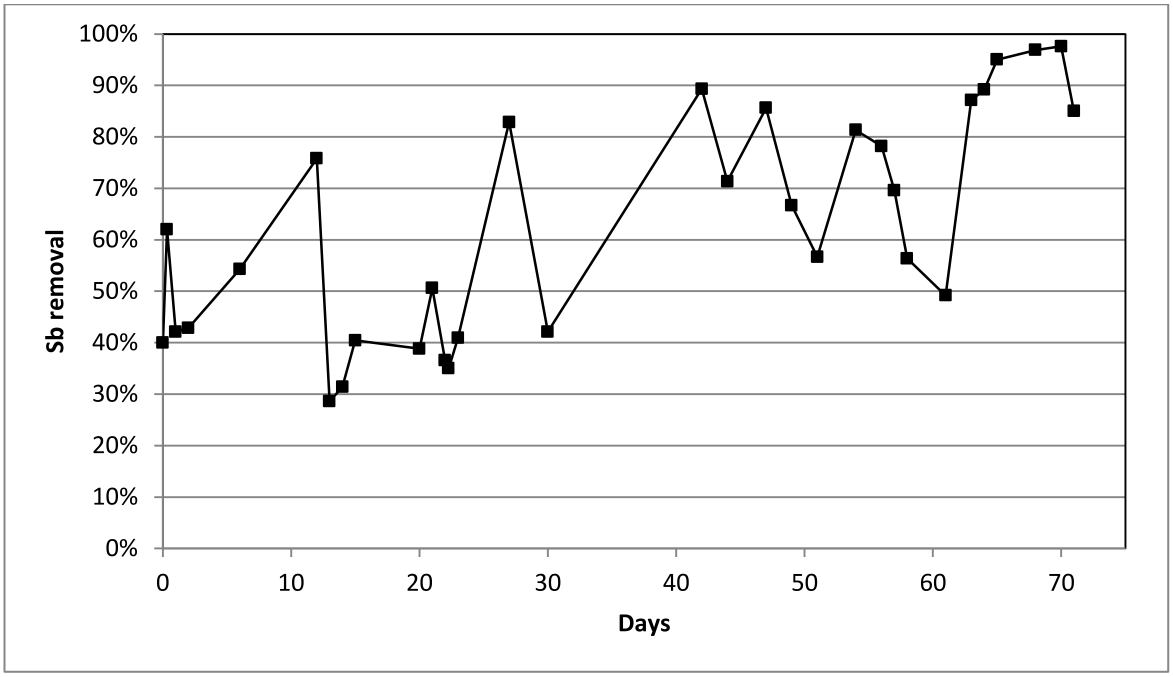

Figure 6 Antimony removal by bioreactor over the duration of the field trials

At HRTs below ~5 h, Sb removal was ~40 %, and at HRTs between 20 and 30 h, Sb removal was up to 98 % (Figure 5). Antimony removal rates ranged from 0.002 moles/m^3/d to 0.034 moles/m^3/d and are correlated with HRT. Solid samples from the bioreactor analyzed by SEM with EDS confirmed the presence of stibnite, suggesting *in situ* sulfate reduction was occurring (Figure 7). Preliminary genomic DNA and RNA-Seq molecular analysis of the substrate shows a complex community of sulfate-reducing bacteria along with species capable of metabolizing intermediate sulfur compounds, such as *Dethiosulfovibrio peptidovorans.*

Removal of Sb with a sulfate-reducing bioreactor may be a better long-term treatment technique than removal through adsorption onto iron oxyhydroxide precipitate. Preliminary work here shows that for similar sized systems, a bioreactor will outperform an adsorption chamber over time.

It should be noted that the duration of this experiment (71 d) was relatively short, and that the bioreactor had likely not reached steady-state conditions. It is possible that, over time, bacteria may reach a rate-limiting phase due to a condition such as complete lignocellulose hydrolysis (Brown, 1983) which could then compromise performance. To determine long-term performance of a bioreactor removing Sb (as well as long-term performance of an adsorption chamber), both systems were restarted and have been operating continuously for nearly two years. Complete data analysis will be presented in another publication, however, preliminary results show generally good performance over this time (Figure 8). Poor performance between days 124 and 162 and between days 405 and 483 coincide with cold winter conditions, which could affect the activity of sulfate-reducing bacteria.

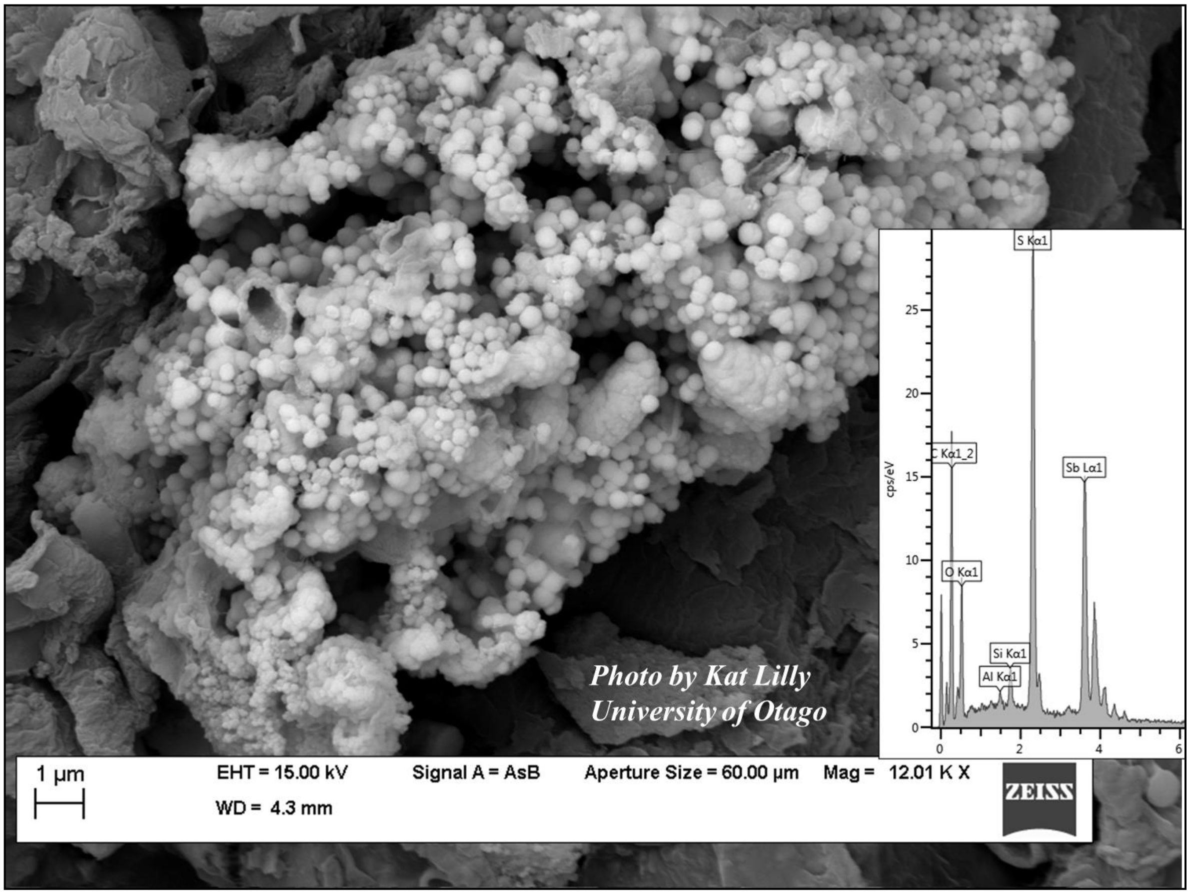

Figure 7 SEM microphotograph and EDS scan of antimony sulfide (stibnite) in substrate from the bioreactor

CONCLUSIONS

These results show that Sb dissolved in mine water can be removed through adsorption onto ferric hydroxide precipitates sourced from coal mine AMD. This study also shows that Sb can be removed through sulfate reduction in a sulfate-reducing bioreactor. For treatment by adsorption, Sb concentrations can be lowered by 14 % at HRTs of only 3 min and by 95 % at HRTs above 2.5 h. Performance declines in an adsorption chamber as the adsorption capacity of the treatment media is approached, therefore, HRT must be extended over time to compensate.

In a bioreactor, treatment of Sb occurs through sulfate reduction and formation of stibnite. Antimony concentrations can be lowered by 81 % at HRTs of only 2 h and by 98 % at HRTs above 20 h. Treatment performance increases with time as the microbial population expands and sulfate reduction improves. Therefore, HRTs should be longer initially and can be lowered as treatment performance improves.

Although this trial was only 71 d in duration, a second trial is underway (now nearly two years in duration) to measure long-term performance of a bioreactor and to determine if a rate-limiting phase may develop as steady-state conditions are approached. Preliminary results show good performance except during cold winter months when biological activity may be suppressed.

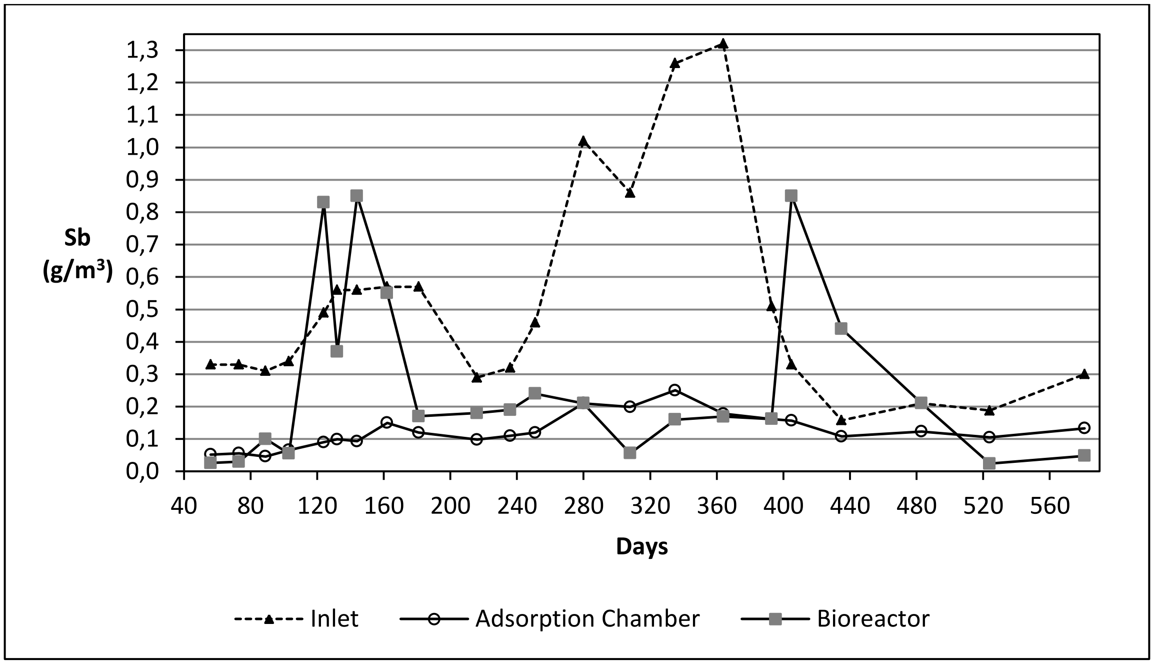

Figure 8 Inlet and outlet Sb concentrations for adsorption chamber and bioreactor over the duration of the second field trial

ACKNOWLEDGEMENTS

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REFERENCES

American Public Health Association (APHA) (2005) *Standard methods for the examination of water and wastewater,* American Public Health Association: Washington, DC, 21st edition.

Biswas, B.K., Inoue, J., Wakakita, H., Ohto, K., and Inoue, K. (2009) Effective removal and recovery of antimony using metal-loaded saponified orange waste. *Journal of Hazardous Materials* **172**, 721–728.

Brown, D.E. (1983) Lignocellulose hydrolysis. *Phil. Trans. R. Soc. Lond.* B300, 305–322.

Cumming, L.J., Wang, L. and Chen, A.S.C. (2007) *Arsenic and Antimony Removal from Drinking Water by Adsorptive Media,* US EPA Demonstration Project at South Truckee Meadows General Improvement District (STMGID), NV Interim Evaluation Report EPA/600/R-07/081.

Kang, M., Kamei, T. and Magara, Y. (2003) Comparing polyaluminum chloride and ferric chloride for antimony removal. *Water Research* **37**, 4171–4179.

Klimko, T., Lalinská, B. and Šottník, P. (2008) Antimony Removal by Zero-valent Iron: Implications for Insitu Groundwater Remediation. *In:* Proceedings of the International Mine Water Association. Karlsbad, Czech Republic. 2–5 June 2008.

Nesbitt, B.E., Muelenbachs, K. and Murowchick, J.B. (1989) Genetic implications of stable isotope characteristics of mesothermal Au deposits and related Sb and Hg deposits in the Canadian Cordillera. *Economic Geology* **84**, 1489–1506.

Nokes, C. (2008) *An Introduction to Drinking Water Contaminants, Treatment and Management,* Environmental Science and Research Ltd, Prepared for the New Zealand Ministry for the Environment.

Rait, R., Trumm, D., Pope, J., Craw, D., Newman, N. and MacKenzie, H. (2010) Adsorption of arsenic by iron rich precipitates from two coal mine drainage sites on the West Coast of New Zealand. *New Zealand Journal of Geology and Geophysics* **53**, 179–195.

Trumm, D. and Rait, R. (2011) Passive treatment of antimony using AMD precipitates and through sulfate reduction. *In:* Proceedings of the 44th annual conference, New Zealand Branch of the Australasian Institute of Mining and Metallurgy. Queenstown, New Zealand. 27–30 August 2011.

Williams-Jones, A.E. and Normand, C. (1997) Controls of mineral parageneses in the system Fe–Sb–S–O. *Economic Geology* **92**, 305–324.

Wilson, N. and Webster-Brown, J. (2009) The fate of antimony in a major lowland river system, the Waikato River, New Zealand. *Applied Geochemistry* 24, 2283–2292.