# The influence of engineering scale on the performance of compost bioreactors for the remediation of divalent metals

Catherine J. Gandy, Adam P. Jarvis

Hydrogeochemical Engineering Research & Outreach Group, School of Civil Engineering & Geosciences, Newcastle University, UK, catherine.gandy@newcastle.ac.uk

**Abstract** The effects of engineering scale on the performance of a compost-based system for the remediation of a discharge from an abandoned metal mine in Cumbria, UK, has been investigated by the simultaneous operation of laboratory-scale columns, under both controlled laboratory and field conditions, and a pilot-scale system. Clear differences in the performance of the systems are seen, demonstrating the importance of environmental conditions and engineering scale. Early indications are that temperature, in particular, plays an important role in the attenuation of zinc within such systems. Implications for full-scale design of these treatment systems are discussed in this paper.

Key Words engineering scale, metals, compost, treatment

#### Introduction

Compost bioreactors for the remediation of divalent metals (e.g. zinc, lead, cadmium), which occur in discharges from abandoned metal mines, have received much research attention in recent years. Unlike iron, these metals are not readily removed by the generation of (oxy)hydroxides in aerobic wetlands since their hydroxide solubility products are higher and therefore they require a higher target pH in order to be removed in this way (Diaz et al. 1997). In contrast, the solubility products of the sulphides of these metals are lower than that of iron and therefore bacterial sulphate reduction (BSR) in compost bioreactors may offer a more feasible approach to removing such metals at the pH values typically achievable in passive treatment systems, and in timescales that result in reasonably sized systems given limited land availability in the UK. The process is based on the reduction of sulphate, under anoxic conditions, by BSR, which consumes protons (reaction 1), generates alkalinity (reaction 2) and simultaneously releases sulphide to form a precipitate with divalent metal ions (reaction 3) (Walton-Day 1999).

 $2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$  (1)

$$SO_4^{2-} + 2CH_2O \longleftrightarrow H_2S + 2HCO_3^{-}$$
 (2)

$$H_2S + M^+ + 2HCO_3^- \rightarrow MS + 2H_2O + 2CO_2 \quad (3)$$

Other mechanisms which may immobilise metals in treatment systems, such as adsorption and co-precipitation, may simultaneously take place alongside the bacterial sulphate reduction.

Although examples of full-scale compost bioreactors exist in the UK they are based on the removal of iron from coal-mine drainage (Younger *et al.* 2002). The majority of studies into the removal of divalent metals prevalent in metal mine discharges, such as zinc, lead, cadmium, have been undertaken at laboratory-scale and, as such, do not account for variations in engineering scale and environmental conditions at actual mine sites. A short review of the treatment performance of these systems reveals that the area-adjusted removal rate of zinc is typically very low (less than 0.5 g/m<sup>2</sup>/d) compared to that for iron in treatment wetlands for coal mine drainage (on average, iron is removed at an area-adjusted removal rate of 10 g/m<sup>2</sup>/d). Therefore, significant land area would be required for the equivalent attenuation of zinc. Given the upland locations, and consequently steep topography, of many metal mine discharges in the UK, land availability for such systems represents an important consideration (Mayes et al. 2009).

The overall aim for the remediation of these metals is therefore effective passive treatment within a reasonable land area (the latter necessitates a target residence time of 24 to 48 hours). In order to achieve this, BSR needs to be maintained at sufficient rates. Currently, this is one of the biggest problems in the operation of such systems and appears to be linked to the availability of carbon within the compost substrate which is a crucial requirement for sulphate reducing bacteria (SRB) to metabolise. The majority of recent research has focussed on identifying suitable carbon sources for maximising rates of BSR (e.g. Bilek 2006; Costa et al. 2009; Nevatalo et al. 2010) but, together with maintaining high rates of removal, it is important before full-scale systems are commissioned to understand issues of engineering scale.

This paper investigates the effects of engineering scale on the performance of compost bioreactors for the remediation of a discharge from an abandoned metal mine at Nenthead, Cumbria, UK. The simultaneous operation of laboratory-scale columns, both under controlled conditions in the laboratory and under field conditions, and a pilotscale system, has allowed issues of engineering scale and environmental conditions to be studied. The three systems contain identical reactive substrate comprising limestone gravel, compost, wood chips and activated sludge from a municipal wastewater treatment plant, and were designed to have an initial hydraulic residence time of approximately 19 hours. The mine water contains around 2 to 2.5 mg/L zinc and has a circum-neutral pH of 7.5 to 8. The laboratory column is fed by mine water collected from the discharge at Nenthead and has a flow rate of approximately 1.7 mL/min. Both the laboratory-scale column operated under field conditions at Nenthead (field column) and the pilot-scale system are fed by mine water pumped directly from the discharge (note that pumping is for experimental purposes only, it is envisaged that full-scale systems would be gravity fed). The field column has a similar flow rate to the laboratory column (approximately 1.6 mL/min) while the pilot-scale system has a flow rate of around 1.1 L/min.

### Methods

Water samples from the influent and effluent to each system were collected in pre-washed polypropylene bottles on a weekly basis. One aliquot of 30 mL was acidified with 1% v/v concentrated nitric acid for cations analysis whilst a second, un-acidified, sample was collected for anions analysis. A third aliquot of 30 mL was passed through a 0.45 µm filter and acidified with 1% v/v concentrated nitric acid to measure filtered cation concentrations. In addition, a further 30 mL of sample was passed through a 0.45 µm filter into a glass bottle and acidified with 1% v/v hydrochloric acid for DOC analysis. All samples were stored at 4°C between collection and analysis. Cations analysis was performed using a Varian Vista-MPX ICP-OES while anion concentrations were determined using a Dionex DX320 ion chromatograph. DOC analysis was performed using a Shimadzu TOC-5050A analyser. Measurements of water temperature, pH, Eh and electrical conductivity were made at the time of sample collection using a Myron L 6P Ultrameter, calibrated prior to each sampling trip. Total alkalinity was also determined at the time of sample collection using a Hach digital titrator with 1.6N sulphuric acid (pilot-scale system) or 0.16N sulphuric acid (laboratory-scale systems) and a Bromcresol-Green Methyl-Red indicator, with results given in units of mg/L as CaCO<sub>3</sub>.

## **Results and Discussion**

Figure 1 illustrates the influent and effluent total zinc concentrations in the three systems (labora-

tory column, field column, pilot-scale system) during the initial eight months of operation. It should be noted that the influent zinc concentration shown here represents that flowing into the field column and pilot-scale systems and has remained relatively constant at around 2 to 2.5 mg/L (mean 2.1 mg/L). The laboratory column is fed by water collected weekly from the discharge and, despite being preserved at 4 °C, has a slightly lower zinc concentration at the time of sampling (typically 1.5 to 2 mg/L, mean 1.8 mg/L) which is probably a result of some attenuation of zinc during storage (e.g. adsorption / precipitation). Given the similarities in influent zinc concentration, the laboratory column influent zinc concentration is not shown in Figure 1.

Evidently, all three systems are performing as intended and a significant reduction in zinc concentration is observed. The greatest percentage zinc removal is seen in the laboratory-scale columns which consistently remove on average around 93% of the influent total zinc. The results for the field column, however, are based on fewer measurements due to problems with the operation of this system during the harsh winter conditions at Nenthead (located approximately 450 m above sea level). The percentage zinc removal in the pilot-scale system has seen greater variation, reasons for which are discussed below, but at the time of writing the system is removing approximately 70% of the influent total zinc. A slightly higher percentage zinc removal is recorded for dissolved zinc (approximately 96% for the laboratory-scale systems and 83% for the pilot-scale system).

There is a clear difference in performance, therefore, between the laboratory-scale systems and the pilot-scale system, despite the same environmental conditions for the field column and the pilot-scale system. This is likely a factor of the different hydraulic conditions between the two scales. In order to investigate the hydraulic performance of the systems further, tracer tests have been undertaken on all three systems to determine hydraulic residence time. As stated above, the systems were designed to have an initial hydraulic residence time of approximately 19 hours but in all systems this had reduced over the first 6 months of operation with a residence time of 14 hours measured in the field column and 8 hours in the pilot-scale system in March 2011. Clearly, together with compaction of the substrate, some preferential flow must be taking place but this appears to be greater in the pilot-scale system than in the field column which may help to explain the better performance of the field column in terms of zinc removal. The apparent propensity for preferential flow in the pilot-scale system is probably a result of it being a down-flow reactor as opposed



*Figure 1* Influent and effluent total zinc concentrations in the lab column, field column and pilot-scale system.

to the laboratory-scale systems which are up-flow reactors, which would encourage preferential flow. Further tracer tests on both the laboratory and field columns and the pilot-scale system after a year of operation may help to confirm this observation.

The most significant parameters when investigating treatment performance are arguably the area-adjusted and volume-adjusted removal rates for zinc within each of the systems. In the pilotscale system, the average area-adjusted removal rate for zinc over the 8 months of operation is 0.4 g/m<sup>2</sup>/day, while the volume-adjusted removal rate is 0.7 g/m<sup>3</sup>/day. It should be pointed out that these figures are based on the flow rate within the system which has varied considerably, principally due to problems during pumping of the mine water from the discharge to the treatment system, e.g. freezing temperatures during winter resulting in reduced flows. At times when the system was flowing at its designed flow rate of 1.1 L/min, areaadjusted removal rate for zinc was up to 0.8 g/m<sup>2</sup>/day and volume-adjusted removal rate was up to 1.4 g/m<sup>3</sup>/day. In contrast, despite the laboratory-scale system in the field also experiencing problems related to reduced flows, the area-adjusted removal rate for zinc for both this system and the laboratory column is higher with an average of 0.6 g/m<sup>2</sup>/day (field column) and 0.5 g/m<sup>2</sup>/day (laboratory column). Similarly, the volume-adjusted removal rate for zinc for these systems is also higher at an average of 1.4 g/m<sup>3</sup>/day (field column) and 1.2 g/m<sup>3</sup>/day (laboratory column). These removal rates are still significantly lower than those typically recorded for the removal of iron in treatment wetlands, which is typically around 10 g/m<sup>2</sup>/day, which clearly has implications for the design of full-scale systems for the treatment of metal mine waters in terms of the land area required.

In addition to the differences in treatment performance related to scale issues outlined above, differences are also apparent due to environmental conditions. In particular, temperature appears to play an important role in the removal of zinc. Figure 2 shows the percentage total zinc removal and the temperature of the effluent water in the pilot-scale system during the initial 8 months of operation. The relationship between total zinc removal and effluent temperature is clearly seen with a reduction in the amount of zinc removed within the system observed as temperature decreased during the winter followed by a subsequent increase in zinc removal as temperature has risen again in recent months. While effluent temperature has varied between 2 and 12 °C, the percentage zinc removal has ranged from 50% to 90%. There are indications from Figure 1 that zinc removal in the field column is also affected by temperature, shown by an increase in effluent total zinc concentration during the same period (November to March) as higher effluent concentrations were recorded in the pilot-scale system. However, this is based on only a few measurements due to the problems mentioned above with the operation of the field column during the win-



Figure 2 Percentage total zinc removal and effluent temperature in pilot-scale system.

ter. Effluent zinc concentrations in the laboratory column, on the other hand (Figure 1), have remained relatively constant due to the controlled temperature conditions under which this system operates.

It is, as yet, unclear why temperature appears to play such an important role in the attenuation of zinc within such systems but it is possibly linked to the maintenance of reducing conditions essential for the development and sustainability of the important microbial communities which act to remove metals as their sulphides by means of bacterial sulphate reduction. Further evidence for this is provided by the redox potential of the effluent water which has varied between -40 and -230 mV in the pilot-scale system, with, in general, the highest redox potential recorded during periods of lowest temperature. In the field column, redox potential has varied significantly but a minimum of -100 mV has been recorded. The laboratory column, operated under controlled conditions, has shown the lowest variation in redox potential, and also the lowest values, with a minimum of -300 mV measured.

## Conclusions

The simultaneous operation of laboratory-scale columns, operated under both controlled laboratory conditions and field conditions, and a pilotscale system has enabled the influence of engineering scale and environmental conditions on the remediation of divalent metals to be investigated. Clear differences in the performance of the three systems are apparent, with both the lab-

oratory-scale columns achieving a higher percentage total zinc removal (approximately 93%) than the pilot-scale system (currently around 70%). Studies of hydraulic residence time suggest that preferential flow is taking place to a greater extent in the pilot scale system than in the laboratoryscale systems resulting in a significantly lower residence time (8 hours) than the initial 19 hours on which the systems were designed and therefore limiting performance. Temperature appears to play a significant role in the removal of zinc with an obvious relationship evident between the percentage zinc removal in the pilot-scale system and the temperature of the effluent water. During colder conditions when effluent temperature dropped as low as 2°C, the percentage zinc removal reduced to around 50%.

Clearly, these issues of both engineering scale and environmental conditions have important implications for the design and operation of fullscale compost-based systems for the remediation of metals. In addition, the relatively low area-adjusted and volume-adjusted zinc removal rates (albeit significantly higher than those reported in the majority of previous studies detailed in the literature) calculated for the pilot-scale system indicates that considerable land area would be required for a full-scale system, which may pose problems given the upland locations of many metal mine discharges in the UK. Future work will focus on identifying suitable carbon sources and the frequency of carbon additions necessary to maximise rates of BSR and maintain high rates of metal removal.

#### Acknowledgements

This research was funded by the UK Government Department for Environment, Food and Rural Affairs and the Environment Agency (Project No.: SC090024/1) for which the authors are grateful. The authors also acknowledge the assistance of Patrick Orme and Jane Davis of the HERO Group at Newcastle University for the collection and analysis of samples and the Nenthead Mines Heritage Centre for providing a suitable location for the pilot-scale system. The views presented in this paper are those of the authors and do not necessarily reflect the views or policy of the Environment Agency.

#### References

- Bilek F (2006) Column tests to enhance sulphide precipitation with liquid organic electron donators to remediate AMD-influenced groundwater. Environmental Geology 49:674–683
- Costa MC, Santos ES, Barros RJ, Pires C, Martins M (2009) Wine wastes as carbon source for biological treatment of acid mine drainage. Chemosphere 75:831–836
- Diaz MA, Monhemius AJ, Narayanan A (1997) Consecutive hydroxide-sulphide precipitation treatment of acid rock drainage. In: Proceedings of the 4<sup>th</sup> In-

ternational Conference on Acid Rock Drainage, Vancouver, British Columbia, 31<sup>st</sup> May-6<sup>th</sup> June 1997, Vol 3:1181—1193

- Mayes WM, Potter HAB, Jarvis AP (2009) Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. Journal of Hazardous Materials 162:512—520
- Nevatalo LM, Mäkinen AE, Kaksonen AH, Puhakka JA (2010) Biological hydrogen sulphide production in an ethanol-lactate fed fluidized-bed bioreactor. Bioresource Technology 101:276–284
- Walton-Day K (1999) Geochemistry of the processes that attenuate acid mine drainage in wetlands. In: Plumlee GS, Logsdon MJ (Eds) The Environmental Geochemistry of Mineral Deposits Part A: Processes, Techniques and Health Issues. Reviews in Economic Geology, Vol 6A:215—228
- Younger PL, Banwart SA, Hedin RS (2002) Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Netherlands, 442 pp