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## BIOREMEDIATION OF ALKALINE MINE EFFLUENT USING TREATMENT WETLANDS

by

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**Introduction.** Decommissioning of metal mine effluent traditionally involved costly chemical applications. Development of passive treatment systems, employing both biotic and abiotic components has been recognized as a cost-effective, ecologically favorable approach in the last decade. This paper documents construction of the first (experimental) treatment system in Ireland at a large lead-zinc mine, attempting to promote adoption of this innovative treatment alternative for future applications.

Additional Key Words: sulfate, heavy metals, vegetation

### Materials and Methods

#### Design and Experimental set-up

Two experimental systems were constructed at an active lead/zinc (Tara Mines) mine near Navan, Ireland, to treat seepage effluent enriched with sulfate and heavy metals. Each system comprises three 16 m<sup>2</sup> (2m depth) in-series surface flow (SF) ponds, viz., inflow, vegetated and outflow, which are filled with spent mushroom substrate (SMS) and a fine inert grit, by volume of 1:6 (inflow and outflow, 30cm depth) and 1:3 (vegetated, 0.5m depth). For more details see O'Sullivan *et al.* (2000).

#### Sulfate and metal analyses

Sulfate in water was measured by Ion Chromatography using Dionex instrumentation (QIC analyzer, automated sampler and 4400 integrator, Sunnyvale, CA) equipped with a separator column and conductivity cell. Algae and plants were digested overnight in strong acid under high temperature, using Teflon™ bombs as described by Beining and Otte (1996). Lead, zinc and iron were analyzed in extracts and water using an Unicam 929 Atomic Absorption Spectrophotometer supporting SOLAAR ATI software. Concentrations were log-transformed to obtain homogeneity of variance. Data were analyzed using SAS

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to test for differences which were significant by conducting a series of ANOVAs.

### Results and Discussions

#### Water characteristics

Process mine water concentrations supplied to the experimental wetlands typify sulfate, zinc and lead of 900 mg L<sup>-1</sup>, 5.0 mg L<sup>-1</sup> and 0.1 mg L<sup>-1</sup> respectively. Iron and cadmium levels are normally below detectable limits. These metal levels are low compared with typical mine effluents. Considerable quantities of metals released in the mine effluent precipitate in alkaline settling ponds before discharged to the treatment systems. Chemical or hydraulic loading rates are not consistent, consequent of mining operations, yet flow rates ranged between 800 mL min<sup>-1</sup> - 1.5 L min<sup>-1</sup> during the monitoring period. This water has a net alkaline pH due to the buffering capacity of local calcite and dolomite limestone. Preliminary data indicated that the systems equilibrated within one year following construction. These data (Nov. 1997-Oct. 1998) are discussed in detail elsewhere (O'Sullivan *et al.* 1999), but are also included (where relevant) within the context of this paper to highlight differences in operation of the systems before and after equilibration.

#### Reduction of metals in water

Generally, zinc and lead exhibited consistent and greater removal rates after the equilibration phase (Table 1). System 2 displayed consistently better reduction rates for both metals (Zn: 94-99%, Pb: 25-

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60%) compared with system 1 (Zn: 0.99%, Pb: 0.64%). Since lead levels supplied were small, it is possible that differences in concentrations entering and exiting were not highlighted and hence did not accurately reflect removal patterns. Reduction as a function of loading concentration yielded correlation (not presented) coefficients ( $r^2$ ) for both metals with Zn = 0.99 and Pb = 0.97. These coefficients may imply linear removal rates within the systems' treatment capabilities. This indicates that variable removal rates may be attributed to loading levels, rather than to season in these systems. Furthermore, W 2 received stronger effluent than system 1, possibly accounting for improved removals.

#### Reduction of metals in algae and plants

Reductions in Zn (92%), Fe (97%) and Pb (59%) were measured in algae tissues sampled within the treatment systems. System 2 exhibited greater reduction between wetland (W) and final (Out) cell tissues compared with system 1, probably because algae failed to colonize the inflow cell (O'Sullivan *et al.* 2000). Zinc accumulated in plants, mainly roots, over time ( $p < 0.05$ ) while trends for lead and iron were not significant. Plants measured higher metal levels in shoots during non-growing seasons. This effect was more pronounced for *Phragmites* than for *Typha*. These data suggest metal uptake by plants from prevailing contaminated waters was linear, although fractions were not translocated to shoots except during dieback periods. Possibly inherent exclusion mechanisms, generally restricted metal transfer to shoots, while some species have evolved compartmentalization techniques administering more concentrations to senescing leaves. Additionally, metal fractions adhering to iron-hydroxide precipitates, which form in locally oxidized root zones, may account for greater root-shoot concentrations.

#### Sulfate removal in water

Sulfate removal from water circuits in both treatment systems improved after equilibration. Absolute removal rates reached  $29 \text{ g m}^{-2} \text{ day}^{-1}$  (69% in December 1998). Non-growing seasons displayed improved performance ( $p < 0.001$ ), in conjunction with highly reduced (-444 Eh) rhizospheres (O'Sullivan *et al.* 2000). These trends were more pronounced for system 2 than system 1, which concurrently exhibited greater sulfate removals. Activity of sulfate reducing microbes (indigenous in SMS) was not apparently inhibited during winter, possibly because seasonal temperature ranges (mild Irish Atlantic climate) did not fluctuate much (4-16°C). Strongly reduced soils and increased organic material in dieback periods may explain improved reduction rates compared to growing seasons, when rhizomes locally oxygenated sediments.

Plant tissues were also analyzed for sulfur fractions, which generally exhibited up to two-fold increases in roots since transplanted, particularly in *Typha*. Auxiliary data for metals and sulfur are presented elsewhere.

**Table 1.** Bulk heavy metal removal rates in water. Values are expressed as  $\text{mg m}^{-2} \text{ day}^{-1}$  and are calculated as differences in water entering and exiting the treatment systems, functional to the average flow rate. Equivalent percentage reductions are indicated in parenthesis,  $n = 5$ . †, \*, \*\*, Statistically significant at the  $>0.05$ , 0.05, and 0.01 levels of probability respectively.

Metal	Zinc		Lead	
	1	2	1	2
System				
Oct. 97	0 (0)*	1.8 (47)**	-0.8 (0)*	-0.7 (0)*
Nov. 97	4.9 (95)**	0.5 (67)**	0.8 (33)†	0 (0)*
Jan. 98	0.3 (50)*	0.5 (67)*	-0.8 (0)†	-0.8 (0)†
Nov. 98	-0.3 (0)*	61.2 (98)**	-3.5 (0)*	0.8 (4)*
Jan. 99	1.3 (99)*	34.0 (94)**	1.6 (48)*	2.5 (60)*
Jun. 99	1.3 (71)**	8.9 (98)**	5.8 (64)*	5.8 (28)**
Mar. 00	5.7 (67)**	70.0 (99)**	1.1 (26)*	6.6 (50)**

#### Conclusions

It is apparent that the experimental systems did not attain their treatment capacity (at least for metals) during the course of this monitoring. This may be due to insufficient and inconsistent chemical and hydraulic loading rates, which correlate highly with removal potential in the literature. Consequently, long-term treatment of sulfate may be jeopardized since substantial metal cations are required to precipitate high levels of sulfate anions. However, if iron levels are sufficient, iron-sulfides may constitute a suitable alternative treatment process.

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