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Chapter 9

Modelling Contamination in an Urban Canal Sediment: Some Preliminary Results from a Phytoremediation Project

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Abstract. Sediments in a derelict section of canal in a former industrial region of North-West England contain a wide range of elevated contaminants including Cu, Zn, Ni, As, Pb, Cd, Cr, mineral oils, TPHs, PAHs and sulphides. Associated costs of disposal have been a constraint to restoration of the canal, which has remained unused for navigation for 50 years or more. On-site phytoremediation is being used in the current project to investigate whether a healthy environment can be restored without extensive removal of the sediment from the site. A raised platform of dredged sediment has been created within the partially drained canal. As the sediment dries and becomes aerated, metal availability was markedly altered and volatilisation rates of organics appeared to increase. Decreasing sulphide/sulphate ratios, lowered pH and altered Fe mobility had differing effects on trace elements. Repeated wetting and drying mobilised a substantial proportion. The project is comprehensively modelling these processes, and aims to demonstrate that metals can be rendered immobile and non-hazardous in soils and biomass whilst plant roots and developing biota optimise conditions for the natural attenuation of organics.

9.1. Introduction

Canals were formerly important transport routes for industry and trade in North-West England. Between Liverpool and Manchester, canals were excavated from

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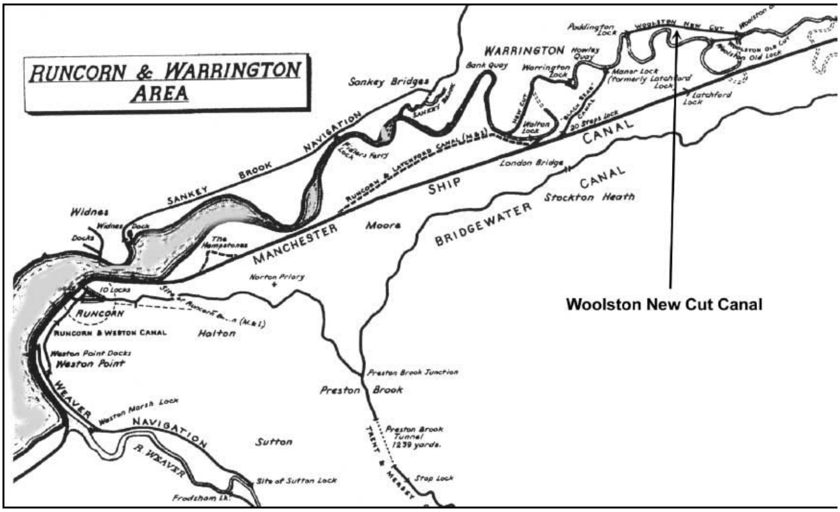

Figure 1: Old map showing extensive canals in the region, including the 2 km section of the Woolston New Cut Canal excavated in 1821 to improve navigation of the River Mersey. Liverpool and the open sea are to the left of the map.

the 18th Century to improve navigation of the River Mersey which links the two cities with each other and to the North Atlantic Ocean (Fig. 1).

The Manchester Ship Canal was excavated in the late 19th Century as difficulties with navigation of the tidal river were losing trade to the new railways. The 2 km section of canal at Woolston, the site of the present study, was excavated in 1821 to shorten large bends in the River Mersey and to improve navigation. The river at Woolston is still subject to tidal influence; water into the canal was formerly controlled by lock gates and by an aqueduct which crossed the river. Industrial development along the Woolston New Cut Canal appears to have been limited to chemical works, a gunpowder factory, a tannery and an abattoir, although adjoining sections of the riverbank have supported various industrial and engineering works, more tanneries, and a gas works. The sediment was undoubtedly influenced by numerous industries and by spillages from ships. Perhaps associated with the demolition of the aqueduct in 1978, the canal has fallen into disrepair and dereliction. The canal ceased to flow, water levels dropped and the standing water and wet sediment has been colonized by vegetation: dominantly *Typha latifolia* (Reedmace), with *Salix atrocinerea* (Sallow) at the edges.

After abandonment, environmental improvement of this derelict section of canal was prohibitively expensive due to the cost of disposal of some 40,000 t of contaminated sediment. From an earlier unpublished consultancy report, it was known that the canal sediment consisted of a wet, black, odorous and oily mud (up to 1.5–1.7 m depth) containing a wide range of elevated contaminants including Cu, Zn, Ni, As, Pb, Cd, Cr, phenols, mineral oils and S. The proportion of bioavailable metals in this type of sediment may be as much as 40% of total concentrations, even after 60 years without disturbance (Stephens et al., 2001). This may present a considerable hazard of dispersal to the wider environment if wet, reduced sediments are disturbed. The context of this current work is the restoration of the canal and adjacent land to community use for recreation and amenity, whilst addressing residual contamination issues.

Phytoremediation is receiving considerable attention as a low-cost treatment technology for land and groundwater contaminated with heavy metals (Chaney et al., 1997; Glass, 1999; Vangronsveld et al., 2000; Pulford et al., 2002) and organic compounds (Carman et al., 1998; Meagher, 2000; Campanella et al., 2002; Susarla et al., 2002). One strategy is to use fast-growing trees, particularly *Salix* and *Populus*, to remove, stabilize or enhance the volatilization of polluting chemicals (Jones et al., 1999; Greger & Landberg, 2000; Pulford et al., 2002; Vervaeke et al., 2003). There is a real possibility that plants can be used to reclaim contaminated land and restore sustainable and healthy soils (Kearney & Herbert, 1999; Dickinson, 2000). The project described in this chapter is a case study of the feasibility of using phytoremediation as a low-cost alternative to cart and dump of the contaminated sediment. By modelling this ecosystem, the objectives are to investigate whether metals can be rendered immobile and non-hazardous in soils and biomass, whilst plant roots and developing biota optimise conditions for the natural attenuation of organics.

9.2. Methods

Established vegetation was cleared from a 150 m section of the New Cut Canal bank and from shallow sediment on the side of the canal opposite the towpath. A raised platform (3.5 m wide) above the existing water level was then created along the shallow side, by dredging and transfer of sediment from the towpath side to the shallow side of the canal (Fig. 2). The platform was divided into six experimental blocks. Within each block, 12 short-rotation coppice taxa (species, hybrids or clones) of willows, poplars and alders (Table 1) were each planted in double rows (0.5 m apart), randomly selected, with 1 m between each double row. An additional unplanted space, equivalent to a double row, was left unplanted within each block, as a control. In each row, there were six plants of each taxon, planted 0.5 m apart. *Salix* and *Populus* were planted as pegs, and *Alnus* was planted as 50–70 cm rooted stock (pruned back after establishment).

Three sediment samples (0–15 cm) were taken with an auger between each row, and then bulked for each of the six blocks. The samples were thoroughly

Figure 2: Canal being dredged to create a 3.5 m raised platform within the canal, with double rows of planted trees.

mixed, then evenly divided and delivered to three national UKAS accredited laboratories. A more extensive modified herringbone design was used to sample sediments in order to map spatial variation of metals on the planting platform. The sediment samples were all taken between trees within the planted rows, from four set distances across the width of the planting platform. This provided one sample from within each planted row of six trees, using a modified herringbone design along the length of the platform. Subsequent chemical extractions (*aqua regia*, EDTA and $CaCl_2$) and metal determinations were carried out in-house, with some support from the NERC ICP facility at Royal

Table 1: Tree species and clones planted on the raised platform of sediment in the canal.

Salix viminalis 'Jornn'*
Salix viminalis × *schwerinii* 'Tora'*
Salix caprea × *cinerea* × *viminalis* 'Calodendron'*
Salix viminalis × *burjatica* 'Ashton Stott'*
Salix viminalis × *caprea* 'Sericans'
*Salix fragilis**
Salix atrocinerea[a]
Populus deltoides × *nigra* 'Ghoy'
Populus trichocarpa 'Trichobel'*
Alnus glutinosa
Allnus incana
Alnus cordata

*Recommended for SRC use in FC Inf. Note 17.
[a] From cuttings of trees naturally colonizing canal.

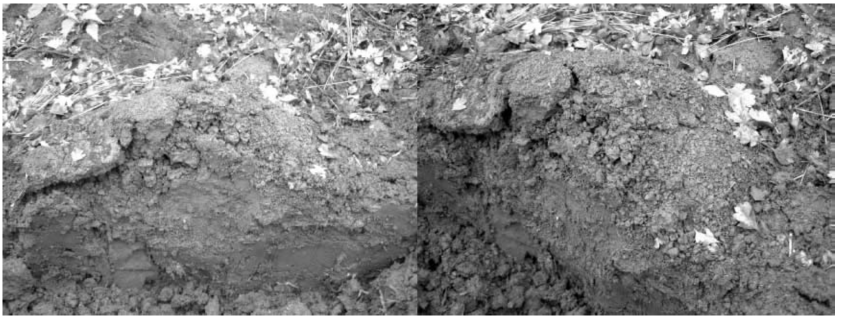

Figure 3: Vertical profiles through surface "puffs" of friable soil, surrounded by more compacted soil on the planting platform. Tree leaves (approx 3 cm length) provide scale.

Holloway. Independent analyses were also carried out using AAS in the Chemistry Department at the University of Glasgow.

After the first year, physical changes in the sediment were apparent. Some areas were flattened through compaction (at least partly through trampling on the platform), but some areas had small upwellings of loosely compacted sediment-referred to here as puffs (Fig. 3). Samples of these two types of sediment were also compared with freshly collected benthic sediment. In this case, metals were extracted using HNO_3/HCl (9:3), 0.05 M EDTA or deionised water, followed by AAS determination of Fe, Zn, Cu, Cd and As (the latter using hydride generation). Additionally, freshly collected air-dried (35°C for 24 h in an air-circulating oven) sediment was re-wetted (5 g sediment in 25 ml deionised water), continuously agitated for 1 hour, and then the filtered leachate was analysed for the same elements. The sediment was then air-dried and the process was repeated eight times. All treatments and analyses were carried out in triplicate. Only selected results are shown in the present chapter.

Five boreholes were established to the side of the canal to monitor groundwater, for analysis by an external laboratory. Establishment of growth of the trees was monitored during the first year, and invasive plants were controlled by hand weeding and herbicide spraying.

9.3. Results and Discussion

The first analyses of the sediments showed considerable variation between laboratories (Table 2). Part of the explanation for these differences concern different analytical methodologies, the details of which were not automatically provided by any of the laboratories. Whilst the three laboratories were UKAS

Table 2: Mean values (mg kg^{-1}) for sediment contamination as provided by separate UKAS accredited laboratories. Values in bold are those exceeding standard contamination thresholds ($n = 7$).

Determinand	**Laboratory**		
	A	**B**	**C**
Sulphate	0.53	0.60	**0.97**
Sulphide	**1078**	354	84.0
Arsenic	**349**	**682**[a]	**1.6**
Boron	**69.0**[a]	**3.5**	1.6
Cadmium	**12.7**	**13.6**	**18.1**[a]
Chromium	**790**[a]	**1471**[a]	**977**[a]
Copper	**567**[a]	**1076**[a]	**736**[a]
Lead	**1221**[a]	**2150**[a]	**1443**[a]
Nickel	**67**	**78**	**783**
Mercury	**3.8**	**7.5**[a]	**4.8**
Zinc	**3631**	**5835**[a]	**4286**
Cyanide	103[a]	10.6	23.2
Total PAH	**216**[a]	**141**	**121**
TPH	**7636**[a]	**5671**[a]	2207[a]

[a] Significantly different to results of other laboratories.

accredited, standard methods for sample preparation, extraction and analysis vary (Dickinson et al., 2000). Although there is a general consensus as to which determinands exceed existing guidelines and thresholds (such as the recently superceded UK ICRCL guidelines), significant differences existed between the laboratories for every determinand. The only exception was for sulphide where data were very variable between samples; this variability probably masked differences between laboratories. More detailed sediment sampling and analysis in-house showed that mobile pools of metals varied considerably (Table 3).

A particularly large proportion of the phytotoxic metal Zn appeared to be in a bioavailable form. Most Fe was strongly bound in the sediments (Fig. 4), but a decrease in the more mobile fractions was evident in the surface of the sediment as it dried. This change was reflected in an increased amount of oxide-bound Fe (data not shown). The changing chemical conditions reduced the mobility of Cu, probably as it became bound by chemisorption. In contrast, Zn is physisorbed and this metal became more mobile; exchangeable and pore water concentrations of Zn doubled and this metal moved from the surface layers as the sediment dried and oxidized.

Table 3: Range of metal concentration across the planting platform and relative bioavailability in sediment (pH 3.6–5.5).

Metal	**Total concentration ($mg\ kg^{-1}$)**	**EDTA-extractable as % of total concentration**
Cu	418–1,003	0.6–9.6
Pb	776–1,555	1.1–8.9
Zn	1,003–6,565	11.8–46.5
Ni	55–130	5.0–27.4
Cd	6.9–23.8	1.7–20.9
Cr	496–1,081	<1

The preliminary results suggest that some metals, such as Zn, in this canal sediment may cause toxicity to plant growth. Whilst there were visual symptoms of toxicity in the foliage of some plants, establishment and survival were good. Mortality was 22% in the first year, marginally better than is normally expected for short-rotation coppice on clean soils. Interestingly, the least successful species was *S. atrocinerea* (67% mortality); this species had naturally colonized the canal banks and exposed sediment, but appeared to be a difficult species to root from cuttings. Plots containing this species were not replanted, but instead are being maintained free of weeding and herbicide sprays as a "natural regeneration" treatment.

Sediment pH of the highly organic sediment on the planting platform was markedly lower than that of freshly dredged sediment (Table 4). Aeration and drying of the sediment substantially increased sulphate, with increased mobility of metals in sediment from the planting platform, but reduced mobility of As.

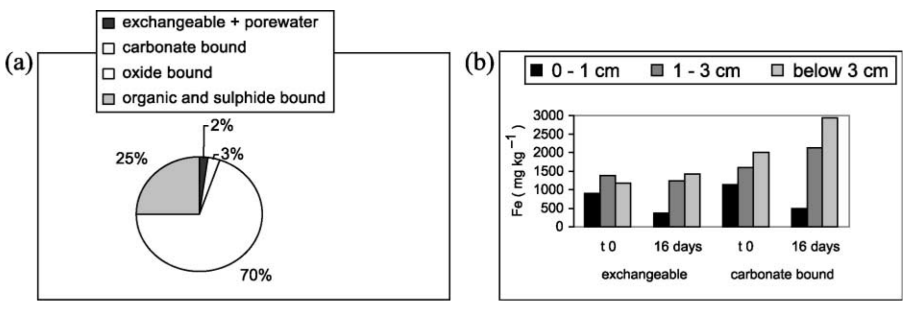

Figure 4: (a) Fe fractionation in freshly dredged wet sediment, and (b) change in the two more labile fractions after 16 days' exposure to air.

Table 4: Analysis of freshly dredged sediment and the two types of sediment on the planting platform.

	pH	Org. matter (LOI %)	Water extracts (mg kg^{-1})					
			SO_4	Fe	Cu	Zn	Cd	As
Benthic sediment	5.7	33.1	83.6	7.18	0.20	2.94	nd	2.50
Planting platform puffs (friable sediment)	3.3	28.6	9,405	114	55.3	29.1	2.71	0.24
Planting platform (compacted sediment)	3.5	31.5	1,190	172	13.5	29.3	1.14	0.78

nd = not detectable.

However, continued wetting and drying of the sediment probably better reflects conditions on the site. The amount of metals in the leachate declined with repeated wetting and drying, as the more labile pools become depleted, Zn became more mobile by about the fifth cycle (Fig. 5).

Using this simple and rather crude method of extraction, a substantial proportion of the total amount of each element was removed from the sediment samples (Table 5). Further work is required to understand how these elements move deeper into the soil profile, and perhaps back to the benthic sediment in the open canal. In the second year the open water had been entirely colonized by *Typha*, where metals would be expected to become immobilized around the roots (Ellis et al., 1994; Ye et al., 1997).

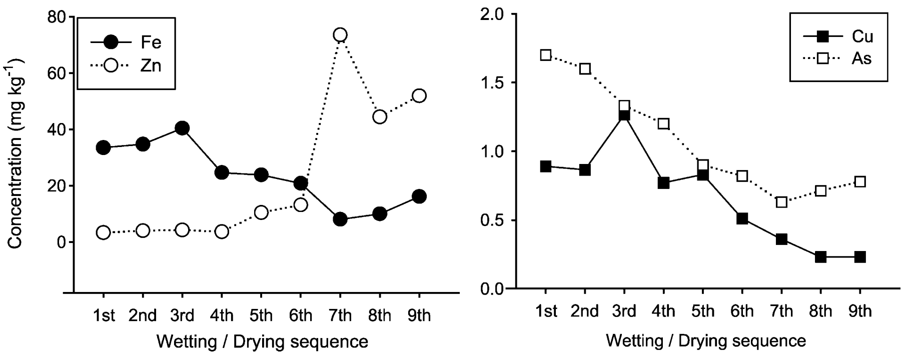

Figure 5: Concentration of elements in leachate after repeated air-drying of freshly-dredged sediment.

Table 5: Element removal from 5 g sediment sample following nine repeated wettings and dryings of freshly-dredged sediment with deionised water.

	Total concentration ($\mu g\ g^{-1}$) in original sample	μg Removed	Percentage of total removed (%)
As	222.3	241.8	22
Cu	96.7	148.3	31
Zn	3899	5216	27
Fe	6661	5303	16

9.4. Conclusions

Since the canal became derelict, the contaminants in the sediment have been maintained in an anoxic, reducing environment. After dredging and exposure to air, the new aerobic and oxidizing environment will undoubtedly induce a host of chemical and biological changes. Sediments deposited on land following dredging have been the subject of previous studies in Belgium (Tack et al., 1996; Tack et al., 1998, 1999; Tack & Verloo, 1999) and the UK (Stephens et al., 2001). Most metals show redistribution from residual to mobile phases during drying and oxidation that is also associated with decreasing sulphide/sulphate ratio. Fe decreases in the surface layers as the sediment dries and becomes aerated and acidified. Mobility of metals clearly differs, but simple experiments showed that 16–31% of elements were fairly rapidly mobilised in water after repeated wetting and drying for 10 days. However, this modelling is in the early stages and more experimental work is required to establish long-term prediction of metal migration.

In the present project, the sediment was retained within the canal banks, and it is likely that migration of metals will be controlled to a large extent by the clay liner of the canal. No elevated metals or organics were recorded in the borehole water after the first year. Nevertheless, before this can become a treatment technology, it is important to demonstrate that contaminants are not quickly dispersed to the wider environment. Another potential source of dispersion is through food chains (Vandecasteele et al., 2002, 2003). Manipulating the processes of contaminant dispersion or immobilisation offers a real possibility of treating contaminated sediment without removal, whilst contributing to a healthy, sustainable, non-hazardous landscape of high ecological and amenity value. One possibility is that sediment disturbance in this way may enhance volatilization of organics whilst actually concentrating metals in a much reduced benthic sediment, within the *Typha* rhizosphere. In turn and if necessary, this lesser amount of sediment and its associated vegetation could be removed at a much reduced cost, compared to disposal of the currently existing sediment. This may be a step towards a realistic, generic and transferable methodology with wide application for cost-effective reclamation of contaminated sediments.

References

Campanella, B. F., Bock, C., & Schroder, P. (2002). Phytoremediation to increase the degradation of PCBs and PCDD/Fs. Potential and limitations. *Environmental Science and Pollution Research International*, **9**, 73–85.

Carman, E. P., Crossman, T. L., & Gatliff, E. G. (1998). Phytoremediation of No. 2 fuel oil-contaminated soil. *Journal of Soil Contamination*, **7**, 455–466.

Chaney, R. L., Malik, M., Li, Y. M., Brown, S. L., Brewer, E. P., Angle, J. S., & Baker, A. J. M. (1997). Phytoremediation of soil metals. *Current opinion in biotechnology*, **8**, 279–284.

Dickinson, N. M. (2000). Strategies for sustainable woodlands on contaminated soils. *Chemosphere*, **41**, 259–263.

Dickinson, N. M., MacKay, J. M., Goodman, A., & Putwain, P. (2000). Planting trees on contaminated soils: issues and guidelines. *Land Contamination and Reclamation*, **8**, 87–101.

Ellis, J. B., Shutes, R. B., Revitt, D. M., & Zhang, T. T. (1994). Use of macrophytes for pollution treatment in urban wetlands. *Resources, Conservation, and Recycling*, **11**, 1–12.

Glass, D. (1999). International activities in phytoremediation. In: A. Leeson, & B. C. Alleman (Eds), *Phytoremediation and innovative strategies for specialized remedial applications* (pp. 95–100). Battelle Press, Columbus.

Greger, M., & Landberg, T. (2000). Use of willows in phytoextraction. *International Journal of Phytoremediation*, **1**, 115–123.

Jones, S. A., Lee, R. W., & Kuniansky, E. L. (1999). Phytoremediation of trichloroethene (TCE) using cottonwood trees. In: A. Leeson, & B. C. Alleman (Eds), *Phytoremediation and innovative strategies for specialized remedial applications* (pp. 101–108). Battelle Press, Columbus.

Kearney, T., & Herbert, S. (1999). Sustainable remediation of land contamination. In: A. Leeson, & B. C. Alleman (Eds), *Phytoremediation and innovative strategies for specialized remedial applications* (pp. 283–288). Battelle Press, Columbus.

Meagher, R. B. (2000). Phytoremediation of toxic elemental and organic pollutants. *Current Opinion in Plant Biology*, **3**, 153–162.

Pulford, I. D., Riddell-Black, D., & Stewart, C. (2002). Heavy metal uptake by willow clones from sewage sludge-treated soil: the potential for phytoremediation. *International Journal of Phytoremediation*, **4**, 59–72.

Stephens, S. R., Alloway, B. J., Parker, A., Carter, J. E., & Hodson, M. E. (2001). Changes in the leachability of metals from dredged canal sediments during drying and oxidation. *Environmental Pollution*, **114**, 407–413.

Susarla, S., Medina, V. F., & McCutcheon, S. C. (2002). Phytoremediation: an ecological solution to organic chemical contamination. *Ecological Engineering*, **18**, 647–658.

Tack, F. M. G., & Verloo, M. G. (1999). Single extractions versus sequential extraction for the estimation of heavy metal fractions in reduced and oxidised dredged sediments. *Chemical Speciation and Bioavailability*, **11**, 43–50.

Tack, F. M., Callewaert, O. W. J. J., & Verloo, M. G. (1996). Metal solubility as a function of pH in contaminated dredged sediment affected by oxidation. *Environmental Pollution*, **91**, 199–208.

Tack, F. M., Singh, S. P., & Verloo, M. G. (1998). Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environmental Pollution*, **103**, 109–115.

Tack, F. M., Singh, S. P., & Verloo, M. G. (1999). Leaching behaviour of Cd, Cu, Pb and Zn in surface soils derived from dredged sediments. *Environmental Pollution*, **106**, 107–114.

Vandecasteele, B., De Vos, B., & Tack, F. M. G. (2002). Cadmium and zinc uptake by volunteer willow species and elder rooting in polluted dredged sediment disposal sites. *The Science of the Total Environment*, **299**, 191–205.

Vandecasteele, B., Lauriks, R., De Vos, B., & Tack, F. M. G. (2003). Cd and Zn concentration in hybrid poplar foliage and leaf beetles grown on polluted sediment-derived soils. *Environmental Monitoring Assessment*, **89**, 263–283.

Vangronsveld, J., Ruttens, A., Mench, M., Boisson, J., Lepp, N. W., Edwards, R., Penny, C., & van der Lelie, D. (2000). In situ inactivation and phytoremediation of metal-and metalloid-contaminated soils: field experiments. In: D. L. Wise, & D. J. Trantolo (Eds), *Bioremediation of contaminated soils* (pp. 859–885). Marcel Dekker, Inc, New York.

Vervaeke, P., Luyssaert, S., Mertens, J., Meers, E., Tack, F. M. G., & Lust, N. (2003). Phytoremediation prospects of willow stands in contaminated sediment: a field trial. *Environmental Pollution*, **126**, 275–282.

Ye, Z. H., Baker, A. J. M., Wong, M. H., & Willis, A. J. (1997). Zinc, lead and cadmium accumulation and tolerance in *Typha latifolia* as affected by iron plaque on the root surface. *Aquatic Botany*, **61**, 55–67.