

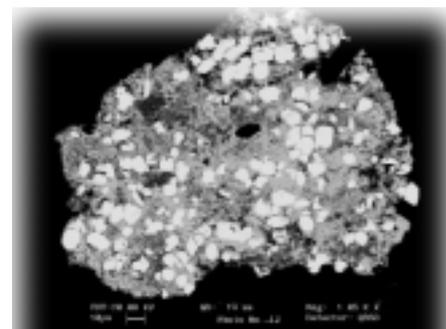
Heavy metals

Contaminants under the microscope

by Neil Fortey, Jonathan Pearce, Antoni Milodowski & Rona McGill, Keyworth

Lead, cadmium, and other toxic heavy metals that are residues of past industrial processes can pose a hazard at brownfield sites in our cities, especially in proximity to housing or on land earmarked for reclamation. These metals may migrate into water supplies or be adsorbed directly by ingestion and inhalation of soil, so the hazard they pose is related to the way in which they occur, as well as their overall concentrations. One established way of evaluating this hazard involves attacking a sample with successively more aggressive solvents and measuring the amounts of

metals released at each step. This may reveal, for instance, how much may be leached by groundwater, or how metal-enriched particles may react within our lungs and intestines. It can also indicate how the metals are bound up in minerals, because different minerals will be dissolved at each step, but this involves many assumptions, bearing in mind the variety of natural and man-made substances that might be present. To gain a better understanding of these processes, mineralogical techniques are being used to study the particles enriched in heavy metals found in soils and contaminated canal mud.



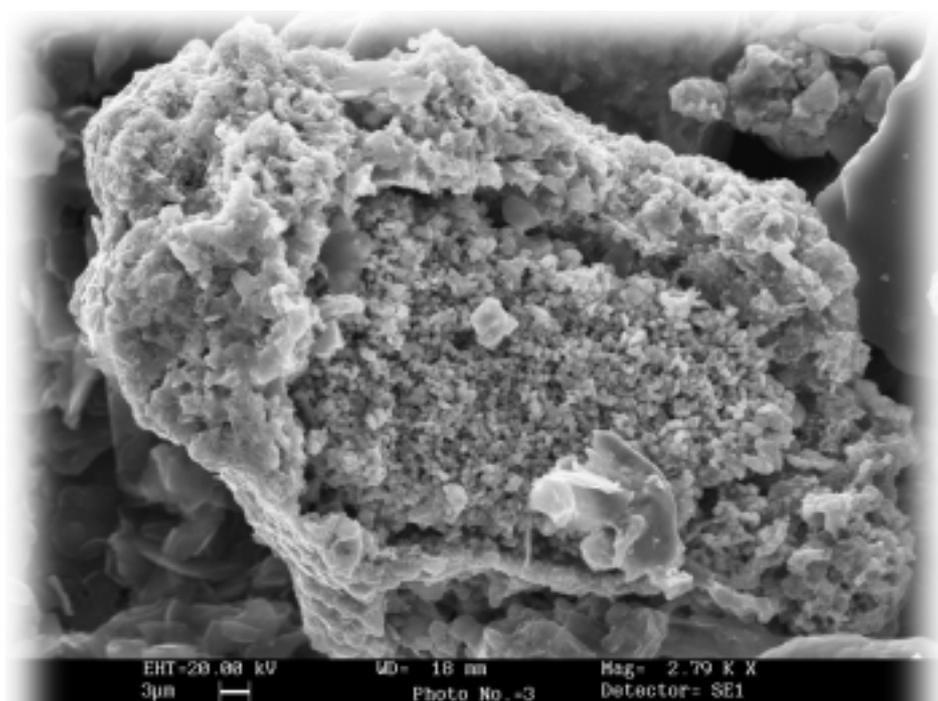
Jonathan Pearce, BGS © NERC

Weathered particle of lead solder from contaminated brownfield soil (Backscattered electron image, field of view approximately 0.25mm across).

Soils taken from contaminated sites in Wolverhampton and Nottingham during the NERC URGENT Project 'Lead Speciation and the Remediation of Brownfield Sites in Urban Areas' are being investigated by scanning electron microscope (SEM) to determine the morphology and composition of lead-enriched particles. The microscopist is confronted with a large number of dense soil particles, few of which are actually enriched in lead. Back-scattered electron images and automated image analysis are used to locate the densest particles, which are then analysed by X-ray spectrometry. This confirms that many are indeed lead-rich, although other dense particles, e.g. barium sulphate, are common.

The compositions and morphological features give clues as to the origins of the particles, so that they can be classified as metallic slag, paint, metallic lead, lead sulphide, and so on. In this way, we are able to build up a precise record of the number and origins of the lead-rich particles in the soil. Moreover, this particle-by-particle approach allows us to use other instruments to determine more diagnostic factors of their composition. In particular, individual grains can be ablated (vaporised) using a laser, and the vapour analysed by mass spectrometer to determine lead isotope ratios. Results from this indicate that the grains contain mixtures of relatively non-radiogenic lead, possibly derived from Australia, and more radiogenic lead, derived from orefields in the British Isles.

Although these dense particles are likely to be difficult to dissolve in soil waters, they often preserve evidence of the

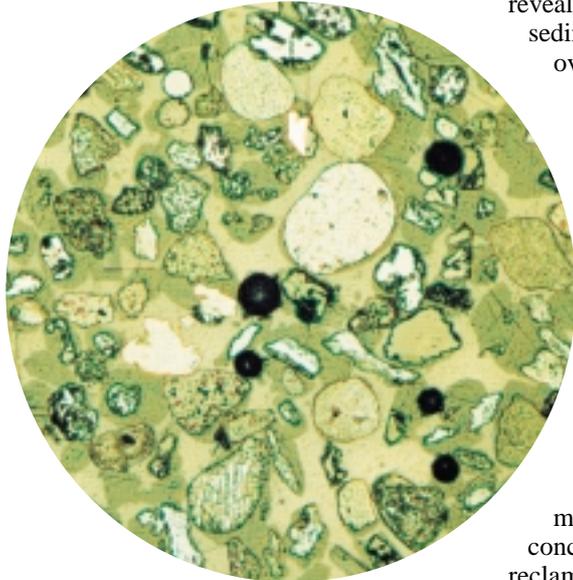


Metallic slag particle from contaminated brownfield soil (SEM image, field of view approximately 85 microns across).

reactions that develop more 'mobile' forms. We need to study in greater detail how lead is bound up in the lighter and most fine-grained fractions, including the respirable PM10 particles (particles less than 10 microns in aerodynamic diameter). Moreover, although these techniques are applicable to relatively abundant heavy metals, such as copper

mineral grains and micro-organisms were entombed. Clays and other minerals were readily observed together with minerals forming in the mud, including calcite, the ferrous phosphate vivianite, and iron, copper, and zinc-rich sulphides. Bacteria were observed along with tenuous webs of biofilm that bind the mud together. Many such films are coated with sulphide deposited by the bacteria. The presence of vivianite reveals that phosphate is bound up in the sediments, restricting its release to overlying canal water and reducing the risk of excessive biological activity such as poisonous algal blooms. At the rural site, where the mud is less phosphatic, iron sulphide is abundant, with spectacular instances of framboid clusters of iron-sulphide particles. Filaments of biofilm were observed attached to the external surfaces and within the pore spaces of the framboids.

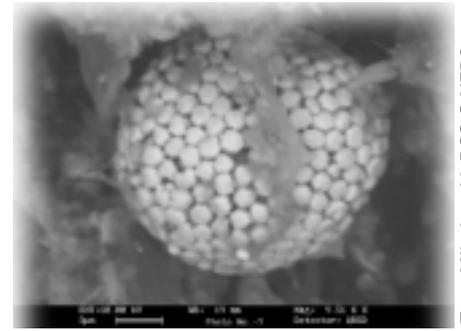
These examples illustrate the expanding role of environmental mineralogy. Our current work is concerned with dust and particles from reclamation of industrial sites in South Wales (see the article on page 15) and other potential applications are being considered. We welcome your suggestions and enquiries.



Metal shards in fragments of brownfield soil (optical image of polished section). Field of view approximately 0.5 millimetres across.

and zinc, investigation of the trace metals, such as cadmium, in soil particles requires different techniques such as ultra-trace analysis by laser ablation.

Another application uses the ability of the scanning electron microscope to observe micro-organisms and undisturbed structures in metal-contaminated canal sediment. In a study led by Dr David Large of Nottingham University, stagnant mud was sampled from canals in the industrial West Midlands and rural Leicestershire. The industrial examples contained high concentrations of phosphorus and heavy metals derived from past industries and sewage discharge. Analyses at the university had indicated the extent to which the metals could be extracted, but mineralogy was needed better to understand their behaviour. Samples were cooled very rapidly by liquid nitrogen so that the water in them turned to an ice-glass in which the



Iron sulphide framboid and strands of biofilm in frozen canal mud (Backscattered electron image, field of view approximately 25 microns across).

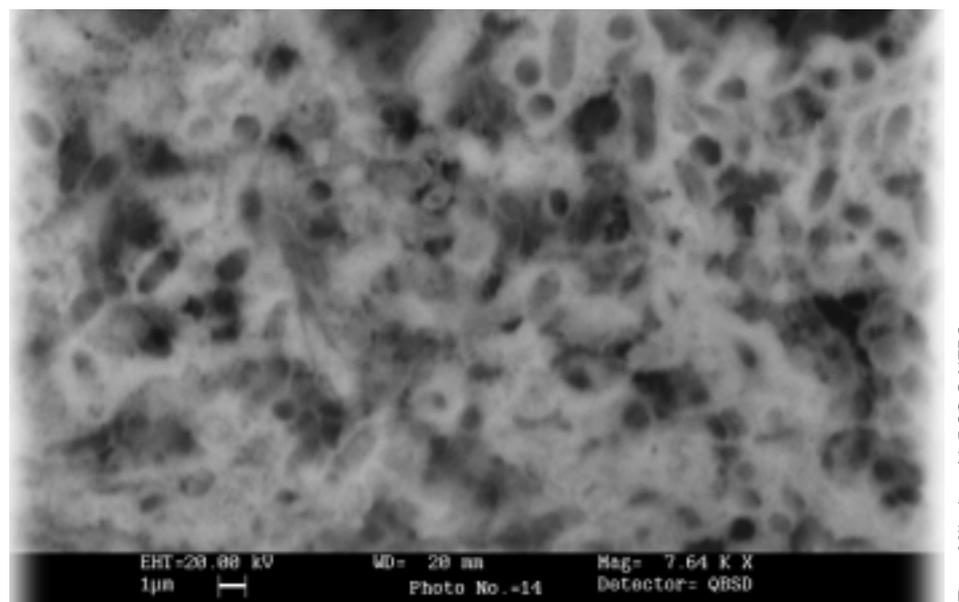
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Bacteria embedded in sulphide-coated biofilm in frozen canal mud (Backscattered electron image, field of view approximately 35 microns across).