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Metal and oxalate contamination in a suburban watershed in the greater Toronto area: The benefits of combining acid leach and selective extraction procedures

B.J. Smith*, J.J. McAlister, H.M. Roe, S.A. Royle

School of Geography, Archaeology and Palaeoecology, Queens University Belfast, BT7 1NN, UK

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ABSTRACT

Environmentally available concentrations of Fe, Mn, Zn, Cu, Pb, Cr and Ni in soils and sediments from a small suburban catchment, obtained using an acid leach procedure, are compared to the Ontario Ministry of the Environment lowest effect level (LEL) and severe effect levels (SEL) and to Provincial sediment quality guidelines (PSQG's). These data are then compared to the bioavailability, potential bioavailability and non-bioavailability of the same metals, plus oxalate concentration, identified using a selective extraction procedure. This combination of techniques enhanced analytical interpretation with respect to metal mobility and potential metal contamination. Selective extraction highlighted the presence of oxalate as a potential contaminant, especially in poorly drained valley floor deposits (33,633 mg kg^{-1} and 26,284 mg kg^{-1}) and lakeshore sediments (27,095 mg kg^{-1} and 13,729 mg kg^{-1}). These levels are considerably in excess of those previously documented in a similar study from Rio de Janeiro, where contamination of urban sediment by sewage is a recognised environmental problem, and could possibly be used both as an indicator of similar contamination and the identification of those areas that warrant further investigation.

1. Introduction and background

Watersheds are increasingly used as the basis for water management policy decisions by both academic and community groups in Canada (Rothwell, 2006), highlighting their amenity value and striving to ensure a healthy ecosystem (Lloyd et al., 2002; Meyer et al., 2005). Within this context it has been recognised that urbanisation (urban sprawl) in metropolitan areas in the Ontario region of Canada, especially parts of Toronto, poses a significant and a growing risk with respect to environmental pollution at the watershed level (Rothwell, 2006). This is linked especially to metals in urban sediments that are washed through watersheds and trapped within the many lakes that act as effective sediment sinks within the once glaciated landscape of southern Ontario. Metals have been identified as amongst the most ecotoxic and challenging pollutants with respect to ecological assessment studies (Huijbregts et al., 2000; Payet and Jolliet, 2002), and it is because of this that answers are required to questions of how metals, and other pollutants, can be more effectively managed in terms of their retention across watersheds and within streams and lakes (Grimm et al., 2005; Groffman et al., 2005).

Sediments in urban and suburban watersheds typically include a range of fine material such as clay minerals derived from soils, carbonates, pollen, algae and fungi. This fine material is particularly efficient at adsorbing metals that are released from, for example, fossil fuel combustion, industrial processes, construction works and the movement and abrasion of mechanical parts in machinery (Neto et al., 1999; Forstner and Wittmann, 1983; Watts and Smith, 1994; Sezgin et al., 2003; McAlister et al., 2005). This is especially the case where sediment is temporarily stored in potentially pollutant rich locations such as on road surfaces, in gulley pots and in sewer systems before eventually reaching either a river channel or lake. As catchments are urbanised, it is also the case that the area covered by impervious surfaces such as asphalt, concrete, rooftops and compacted soil surfaces inevitably increases. Such surfaces are often associated with ongoing problems linked to non-point pollution sources and the extent of impermeable cover has been used as an effective indicator of urban impact on streams (McMahon and Cuffney, 2000).

To provide an indication of the potential impact of polluted sediments in Ontario, sediment quality guidelines (SQG's) have been introduced for environmental screening purposes and to provide benchmarks for sediment quality (McDonald et al., 2000). The Ontario Ministry of the Environment also use Provincial Sediment Quality Guidelines (PSQGs) where three levels of toxicity are defined for benthic organisms: a no effect level (NEL), lowest effect level

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* Corresponding author. Tel.: +00 44 0 28 9097 5144; fax: +00 44 0 28 9032 1280.
E-mail address: b.smith@qub.ac.uk (B.J. Smith).

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(LEL) and severe effect level (SEL) (Jaagumagi and Persaud, 1999; Long et al., 1995). The application of this classification is relatively rapid and is designed to highlight the potential for ecological risk (USEPA, 2001). Elsewhere, guidance concerning risk assessment for metals is also provided by the International Council of Mining and Metals (MERAG) and this has been endorsed by the UK Department for Environmental Food and Rural Affairs (Menzie et al., 2009).

There is, however, a potential confusion as to how metal contents should be assessed in an environmental context, given that a proportion of any metal present could be bound so strongly to the sediment, or held so securely within the matrix of a mineral, that it might only be mobilised under the most extreme or specific conditions. Because of this, these components could be viewed as effectively unavailable to the wider environment. It is for this reason, for example, that 'total element analysis', in which sediment samples are completely dissolved in strong acid(s) (e.g. HF/HNO_3/HCl) (Davies et al., 1987; de Miguel et al., 1997; Sezgin et al., 2003), provides a poor basis for assessing the environmental impact of metals in sediments. More important in an exposure context is the relative availability of metals in sediments, which can be expressed in a number of ways. Bioavailability, for example, refers to the proportion of an elements in soil or sediment that is available for uptake by biota (Meyer, 2002; Naidu et al., 2003). Whereas, environmentally available metals are those that can interact with other environmental matrices and which represent the amounts that are available under a particular set of environmental conditions (McGeer et al., 2003). It is for these reasons that so-called acid leach procedures, using less aggressive acid extraction, such as an HNO_3/HCl mix (e.g. USEPA 3051A), have been employed to extract environmentally available metals and have been found to produce consistent and repeatable results when tested against each other (Andersen, 2005).

In addition to what have become standard environmental analyses described above, it is also possible to segregate the phase composition of different metals even further using sequential extraction procedures that were first developed and are still widely used for establishing the relative mobility of metals in sediments (Tessier et al., 1979; Ure et al., 1993; Quevauviller et al., 1994). These techniques have the added advantage that if sediments are examined along a transport pathway, or down a profile within a sediment sink, they may be used to ascertain whether, for example, metals have become more or less mobile as sediments are weathered. These selective measures are in contrast to conventional acid leach and total element analyses that do not discriminate so effectively for relative availability. Because of this, acid leach techniques are useful as screening tools, but ideally should be combined with appropriate selective extraction procedures to determine not only what is present, but also what their potential impacts are.

It is in the spirit of the above requirement that this study sets out to evaluate results from acid leach and selective extraction analyses for concentrations of environmentally available, bioavailable, potentially bioavailable and non-bioavailable Fe, Mn, Zn, Cu, Cr, Ni and Pb from soils and fluvial and lacustrine sediments within suburban Toronto. The results are then compared to Ontario Ministry of Environment values for limited and severe effect levels, in the hope of identifying synergies that can result from combining different analytical strategies. A selective extraction protocol was used to extract these metals from the water-soluble, exchangeable/carbonate, amorphous Mn, amorphous Fe/Mn, organic and residual (siliceous) phases. This technique examines the transformation of metals between bioavailable (water-soluble phase), potentially bioavailable (exchangeable/carbonate phase) and non-bioavailable forms. Like all analytical techniques, selective extraction procedures contain operational problems (Pickering, 1981; Van Valin and Morse, 1982). Selectivity of elements for a specific phase is thermodynamic and specificity differences between numerous methods means that selectivity is difficult to achieve. There is no general agreement as to which solution should be used to extract metals from the various phases since matrix effects are involved in heterogeneous processes. The selective protocol used depends on the aim of the research, type of samples and the metals of interest. Contamination of analyte and instrumentation plus insoluble residue formation may be overcome by using high purity extracting solutions, the correct sample: solution ratio and methods of extraction (Rauret et al., 1989; McAlister et al., 2003; Van Elteren and Budic, 2004). The extraction efficiency for both techniques was examined by plotting XY correlation graphs. Summation of the individual metal concentrations in each phase, except for the residual, was compared with corresponding concentrations from the acid leach procedure and r^2 correlation values were recorded.

In addition to the analysis of metal concentrations in urban sediments, research in Rio de Janeiro, Brazil (McAlister et al., 2000,2005) has shown that inefficient sewage management can also increase the level of other organic pollutants such as calcium oxalate in urban sediments, especially where sewage overflows mix with street sediments. Such contamination is not, however, restricted to cities in developing and transition economies and ongoing sewage disposal problems have been highlighted in Ontario in a series of Ecojustice Reports (McDonald, 2006,2009; Podolsky and MacDonald, 2008; McDonald, 2009). Sewage is, however, not the only potential environmental source of oxalates and calcium oxalate occurs naturally as whewellite ($CaC_2O_4.H_2O$) and weddellite ($CaC_2O_4.2H_2O$), as a by-product of fossil fuel combustion (Saiz-Jimenez, 1989) and both oxalic acid and oxalates are used in bleaches, metal cleaners, paint removers and many household products, and industrially in engraving, lithographic, metallurgic and pharmaceutical processes (Hodgson et al., 1998). Although Weddellite is environmentally unstable it can remain in urinary calculi in the presence of metal cations at 37 °C for several years in dry conditions (Hesse et al., 1976). Previous studies using selective extraction have shown the organic phase within street sediments to contain the highest concentration of oxalate (McAlister et al., 2005), and in response to this, the current study was restricted to extraction in the organic and water-soluble phases, where the latter phase provides an indication of oxalate solubility. If sewage-derived oxalates is to be found in a city such as Toronto, it is most likely to be linked to contamination of soils and sediments by wastewater runoff and sewage from the widespread use of septic tanks that are the principle sewage management system within the wider urban area. In order to characterise urban sediments, explore links between sediment sources and lacustrine sediments, and specifically to evaluate the utility of using sequential extraction compared to an acid leach procedure as an indicator of the environmental availability of metals in sediments, a small watershed in the Toronto suburb of Brampton, Ontario was chosen as a case study (Fig. 1).

2. Study area

The study catchment was selected because it contains a linked pair of retention lakes created as part of a sustainable urban drainage system that acts as an effective sediment sink. Surrounding this is recreational parkland and woodland that acts as a "buffer" between the lake and the surrounding urban development to the west and the east and a major highway and a spur road leading off it to the north. This situation provides the opportunity to investigate a range of land cover and potential contamination sources. In addition to surface runoff from the surrounding urban and recreational areas, an intermittent stream flows via a wooded valley through a marshy