Available online at www.sciencedirect.com

ScienceDirect

Applied Geochemistry 22 (2007) 1344–1358

Applied Geochemistry

www.elsevier.com/locate/apgeochem

The role of grain dissolution and diagenetic mineral precipitation in the cycling of metals and phosphorus: A study of a contaminated urban freshwater sediment

Kevin G. Taylor [a,*], Stephen Boult [b]

[a] *Department of Environmental and Geographical Sciences, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK*
[b] *Department of Earth Sciences, University of Manchester, Oxford Road, Manchester M13 9PL, UK*

Received 23 December 2005; accepted 15 January 2007
Editorial handling by R. Fuge
Available online 30 March 2007

Abstract

This paper describes the detrital mineralogy, early diagenetic reactions and authigenic mineral precipitates for freshwater contaminated sediments deposited in an urban water body (the Salford Quays of the Manchester Ship Canal, Greater Manchester, UK). These sediments contain a mix of natural and anthropogenic detrital grains. Detrital grains are dominated by quartz and clay grains, whilst anthropogenic grains are dominated by metal-rich glass grains, concentrated at a depth of 12–17 cm in the sediment as a result of historical inputs. Sediment porewaters contain significant concentrations of Fe, Mn, Zn and phosphate. Bacterial Fe(III) and Mn(IV) reduction are hypothesised to supply Fe^{2+} and Mn^{2+} to porewaters, with phosphate released from Fe oxide reduction or organic matter oxidation. Petrographic observations indicate that the metal-rich glass grains are undergoing chemical dissolution during early diagenesis, supplying Fe and Zn to porewaters.

The most abundant authigenic mineral in the sediments is vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), containing a significant level of redlingite ($Mn_3^{2+}(PO_4)_2 \cdot 8H_2O$), with minor framboidal pyrite (FeS_2). Electron microprobe analysis shows the vivianite to contain Zn, Cu and Pb, suggesting that vivianite acts as a long-term sink for these metals in this sediment. This implies that authigenic vivianite in freshwater sediments may act as a long-term sink for metals, in a similar manner to sulphides in marine sediments. This study highlights that the nature of detrital and diagenetic mineralogy, in addition to porewater and sediment chemistry, needs to be considered in assessing contaminated sediments.

1. Introduction

The interactions between sediment and water play a major role in the movement and fate of both contaminants and nutrients in aquatic environments. It has long been recognised that contaminant transport in freshwater systems is overwhelmingly associated with the particulate phase (e.g. Trefry and Presley, 1976; Gibbs, 1977; Salomons and Forstner, 1984; Horowitz et al., 1993). As a result, sediments accumulating in aquatic systems are a significant reservoir of contaminants (Horowitz et al.,

---

[*] Corresponding author. Fax: +44 161 247 6318.
E-mail address: k.g.taylor@mmu.ac.uk (K.G. Taylor).

0883-2927/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apgeochem.2007.01.008

1995; Macklin, 1996). This has been exploited to good effect in the documentation of contaminant chronologies from sediment records in aquatic systems (Renberg et al., 1994; Callender and Van Metre, 1997; Hudson-Edwards et al., 1999). However, once deposited and buried sediment-bound contaminants commonly undergo significant geochemical changes over both short-term (days to months) and long-term (years to tens of years) time-scales. A range of post-depositional processes of a physical, chemical or biological nature may lead to the release of contaminants and nutrients to interstitial or overlying waters, and/or the re-precipitation of more stable minerals in the sediment.

Studies in lakes and shallow marine systems have clearly documented the early diagenetic release of contaminants from sediments (Hamilton-Taylor et al., 1996a,b; Widerlund, 1996; Bryant et al., 1997; Rivera-Duarte and Flegal, 1997; Gill et al., 1999). In many of these studies, the resulting flux of contaminants out of the sediments into overlying waters has been estimated to be of the same order of magnitude as runoff input (Rivera-Duarte and Flegal, 1997; Shine et al., 1998; Covelli et al., 1999). Equally, the release of P from sediments during early diagenesis has been recognised to be an important control on water quality in freshwater systems (Carignan and Flett, 1981; Jensen et al., 1992; Hupfer et al., 1995; Gonsiorczyk et al., 2001). As diagenesis proceeds, a build up of porewater-solutes may lead to mineral saturation, resulting in the precipitation of authigenic sulphide, carbonate and phosphate minerals. These precipitates may also sorb or co-precipitate trace metals, thereby acting as long-term sinks for contaminants in sediments. For example, early diagenetic sulfides have been shown to act as sinks for the metals Cu, Pb and Zn (Parkman et al., 1996; Pirrie et al., 1999).

Although the importance of diagenesis in modelling contaminant cycling and risk assessment has been recognised, most models and assessments are based upon porewater and bulk sediment chemistry data. There have been few attempts in contaminated sediment assessment to integrate the mineralogy and geochemistry of detrital grains and diagenetic mineral precipitates with porewater and sediment chemistry. Such an approach is critical to fully understanding the host species for contaminants and the minerals controlling contaminant release or uptake. This paper describes the nature of the grain-specific geochemistry and mineralogy, together with the sediment and porewater chemistry, in heavily contaminated freshwater sediment deposited in a major urban water body (the Salford Quays of the Manchester Ship Canal, Manchester, UK), and documents the key role that the dissolution of detrital anthropogenic grains and the precipitation of early diagenetic minerals play in metal cycling. Urban water bodies, including canals, docks and lakes, are important components of urban catchments (e.g. Bromhead and Beckwith, 1994; Charlesworth and Foster, 1999; Dodd et al., 2000; Qu and Kelderman, 2001; Hu et al., 2001). They are commonly heavily modified and receive significant amounts of anthropogenic particulate material. The study presented here not only contributes to methods of contaminated sediment assessment, but also provides information on the poorly studied urban sedimentary system.

2. Study site

The contaminated sediment described in this study is from the Salford Quays, an urban water body which was originally the docks at the end of the Manchester Ship Canal (MSC), Greater Manchester, UK (Fig. 1). The MSC was built in 1895 to allow for direct shipping access to the City of Manchester Docks. The MSC begins at the confluence of three rivers (Irwell, Medlock and Irk) that form the major drainage conduit for the Greater Manchester conurbation, while in the past combined sewer overflows have supplied domestic and industrial sewage, and road runoff to the canal. The Manchester Ship Canal is up to 8 m deep, steep sided and up to 50 m wide. As a result, flow is slow, and this has led to the accumulation of highly contaminated, organic-rich sediments. These contaminated sediments have caused a range of environmental problems in the past, including water-column anoxia, sediment rafting, noxious-gas generation and metal mobilisation (White et al., 1993; Boult and Hendry, 1995). Growth in the value of urban watersides has led to the redevelopment of Salford Quays, at the Manchester end of the MSC (Fig. 1). Water quality remediation has taken two stages. Firstly, in 1987 the Salford Quays were hydrologically isolated from the MSC, to prevent future contaminated sediment input. However, the highly contaminated sediment was not removed. The high O_2 demand of this sewage-rich sediment, coupled with the steep-sided nature of the Quays, led to the depletion of O_2 within the water column. As a result the Salford Quays basins experienced

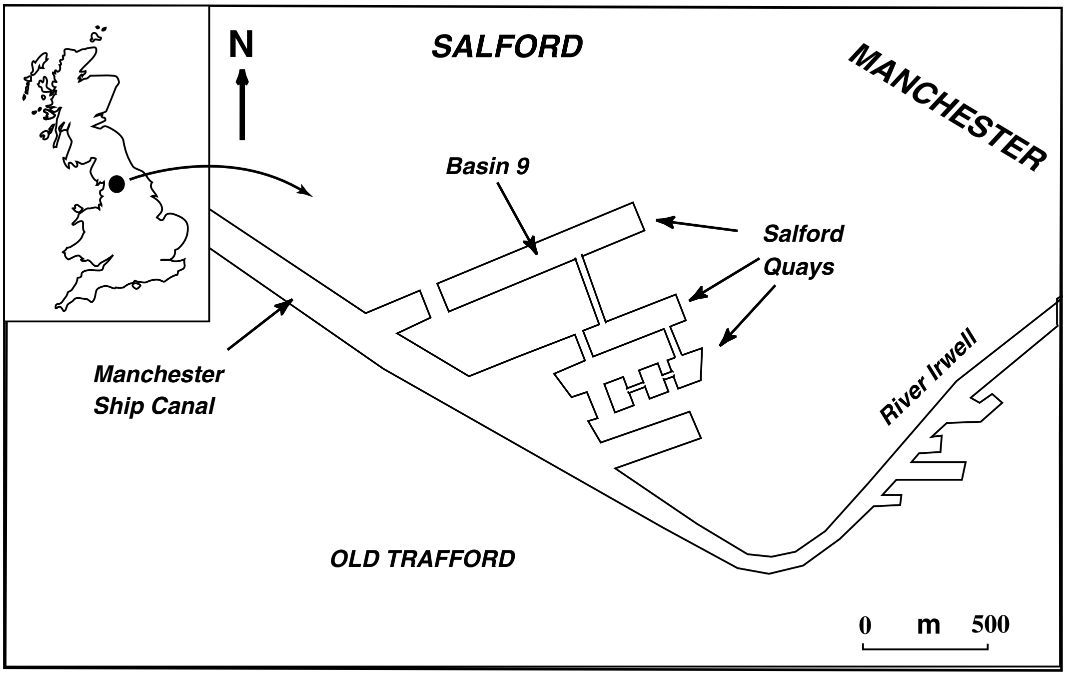

Fig. 1. Location map of Salford Quays and the Manchester Ship Canal, showing the location of Basin 9 where sediments for this study were sampled.

prolonged periods of water column anoxia (White et al., 1993), which was remedied through the use of Helixor pumps to circulate compressed air through the water column and keep water well-mixed (Struthers, 1997). Taylor et al. (2003) documented the bulk chemical and physical nature of sediment change in response to the remediation of the site. The pre-remediation sediment is organic-rich and has high, but variable, metal concentrations. The post-remediation sediment is low in contaminant metals, and dominated by the deposition of autochthonous clays and algal material. Between these two sediments there is a marked layer of high metal enrichment, as a result of the input of industrial waste material into the Quays during the site clearance and remediation period (1987–1990).

3. Methods

Sediment cores were taken on average every six weeks from Basin 9 of the Salford Quays (Fig. 1) over the period March 2000 to March 2001. In total, eight cores were collected and the porewater analysed. Three of these cores were analysed for sediment chemistry and mineralogy. Cores were collected using a 1 m long, 60 mm diameter stainless steel corer, with a stainless steel liner. The corer was pushed into the sediment using lengths of steel rod, and the core retrieved. Sediment was held in the corer barrel by suction. The collected core was split into 1 cm vertical sub-sections by use of a screw-threaded plunger, in a N_2-filled glove-bag to minimise oxidation of reduced species, and samples placed into acid-washed, N_2-purged centrifuge tubes and sealed. Bottom water samples were decanted from the water column immediately overlying the sediments in the core. All sampling was carried out within 2 h of core collection. Porewaters were separated from the solid sediments by centrifugation at 4500 rpm, followed by decantation and filtration again under a N_2 atmosphere. Upon separation, the porewaters were immediately filtered through pre-washed (with 10 mL de-ionised water) 0.2 μm membrane filter papers and split into two aliquots. One aliquot was acidified to pH 2 with a few drops of analytical grade HNO_3 and stored at 4 °C for metal analysis. The other aliquot was analysed for NH_4^+ immediately using an ion selective electrode (DirectIon, Sentek Ltd). Detection limits were 0.1 mg/L NH_4^+, with accuracy ±3%, and precision ±3% of the reading. Sulphate, NO_3^- and PO_4^{2-} were determined in this same aliquot by ion chromatography (IC) using a Dionex Ltd DX-100, within 24 h of sample collection. Detection limits for both anions were 0.1 mg/L. Metal analysis was undertaken on the acidified aliquot by ICP-OES (VG Horizon) with an ultrasonic nebuliser for increased resolution at trace concentrations. Detection limits for Fe, Mn, Zn were 10 μg/L. For all porewaters blanks were run on matrix-matched samples (DIW and HNO_3) which were subtracted from sample analyses. Although no certified porewater reference samples were analysed, matrix-matched standards were made up for the analysis of Fe, Mn and Zn from standard stock solutions. Concentrations of Fe and Mn measured in porewater were significantly above blank levels contributed from analytical grade HNO_3 (<0.00001%), whilst Zn contents were only a factor of 5 higher. All porewater cation and anion concentrations are quoted in μmol/L. Porewater data for all cores analysed were similar, although the length of recovered cores varied. Limited porewater sample volume meant that Eh and pH were not measured.

The solid sediments from each subsample were dried at 105 °C. Pseudo-total metal concentrations were estimated by hot digestion in concentrated analytical grade HNO_3. Sediment (0.5 g) was digested in 10 mL of acid at 85 °C for 2 h. The resulting solutions were filtered using 0.45 μm filters and made up to 50 mL volume with de-ionised water. Metal concentrations in the resulting solutions were determined by flame atomic absorption spectrophotometry (Unicam 929 AAS). Analytical variability was tested by repeating the full analysis on every third sample. Precision was found to be within 5%. Blank samples were analysed throughout. The accuracy of the extraction procedure was determined by analysing certified reference material (stream sediment GBW07311), and was found to be within 10% for all elements. Although many studies utilise a hot aqua regia digest for pseudo-total metal determination, intra-laboratory comparison suggested that hot HNO_3 digest resulted in similar extraction efficiencies for all elements. Inorganic P in the sediment was determined by the method of Aspila et al. (1976). One gram of sediment was digested for 24 h in 1 M HCl at room temperature. An estimate of total P was made on HNO_3 digestate, as for metal determination, recognising that this will not remove all P in the sediment sample. Phosphorus in the resulting solutions was determined by ICP-AES. TOC analyses were determined on one core by analysing acid digested powdered samples in an induction furnace (Leco C/S analyser). Two cores were analysed for metal concentrations, both showing similar contents and profiles. Only the data on one core, for which P and TOC were analysed, are presented here.

Qualitative information on the sediment mineralogy was obtained through the use of whole rock X-ray diffraction analysis of powdered samples, air-dried at room temperature. Samples were run on a Philips PW1050 X-ray diffractometer, using CuKα radiation, with scans taken from 4° to 64° at a scan rate of 2°/min. Whilst poorly-crystalline redox-sensitive phases are prone to oxidation under such conditions (e.g. Nriagu, 1972), the presence of mineral peaks identified in XRD traces, together with observations of well-crystallised phases under SEM observation suggests that these phases do not undergo rapid oxidation. Petrographic and quantitative chemical data were obtained through the use of scanning electron microscopy and electron microprobe analysis. Air-dried samples of sediment were impregnated with epoxy resin and polished surface blocks produced. Petrography on these samples was analysed using a JEOL 5600LV scanning electron microscope using backscattered electron (BSE) imagery. The energy of backscattered electrons is proportional to the atomic mass of minerals, and, therefore, BSE images reveal information about composition. A Link eXL energy dispersive (ED) X-ray microanalysis system was used to obtain semi-quantitative data on major element compositions of mineral grains. Fully quantitative chemical data for both major and trace elements were determined using wave-dispersive X-ray analysis on a Cameca SX100 electron microprobe. Detection limits for trace metals using this technique is on the order of 100 ppm.

4. Results

4.1. Porewater composition

Porewater concentrations for SO_4^{2-} and NO_3^-, NH_4^+, Fe, Mn, Zn and PO_4^{2-} for one core are shown in Fig. 2. Both SO_4^{2-} and NO_3^- have concentrations in the water column of 750 μmol/L and 40 μmol/L, respectively, but rapidly fall to zero beneath the sediment-water interface, whilst NH_4^+ displays a gradual increase with depth, from below detection in the water column to 3000 μmol/L 15 cm below the sediment-water interface. Ferrous iron and Mn^{2+} increase in the porewaters from a level below detection in the overlying water column. Porewater Mn rapidly increases to a value of 25 μmol/L within

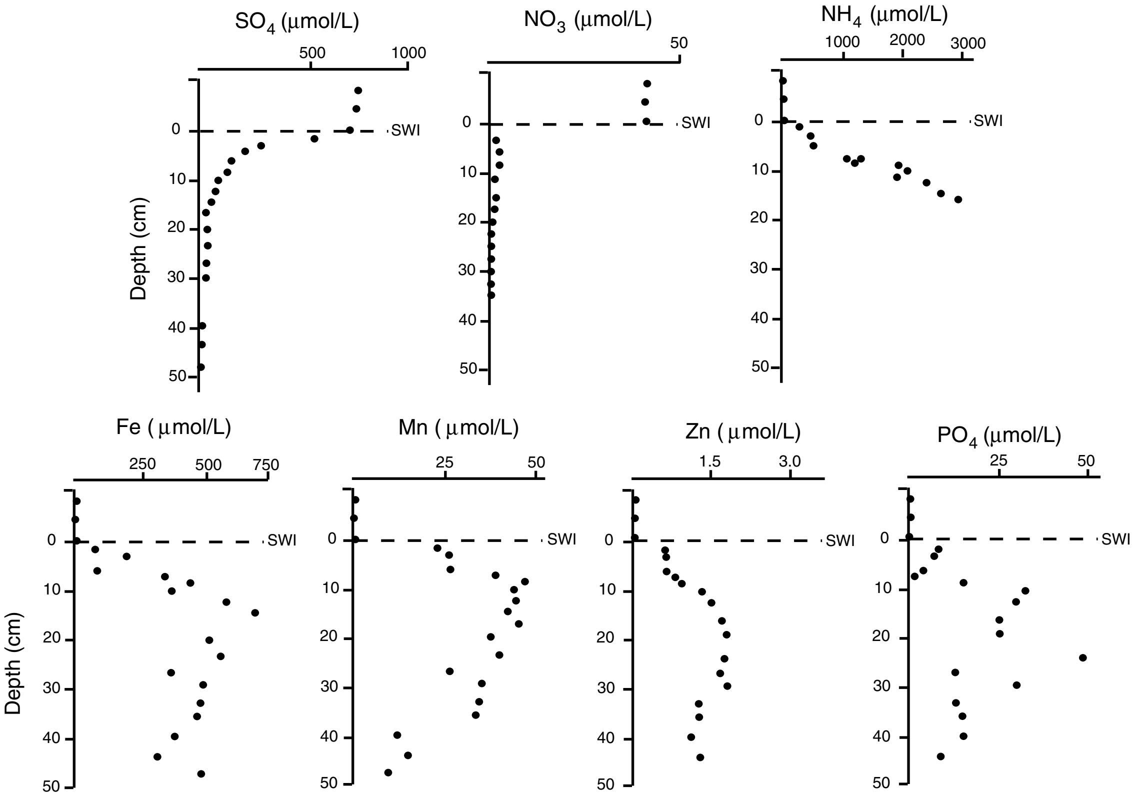

Fig. 2. Porewater and bottom-water concentrations of SO_4, NO_3, NH_4, Fe, Mn, Zn and PO_4 for sediments and water from the Salford Quays study site. Depths indicated are metres below the sediment–water interface (SWI).

2 cm of the sediment-water interface, and then exhibits a more pronounced peak of 50 µmol/L at 12–15 cm depth. Beneath this, Mn concentrations decrease with depth, with levels approaching the limits of detection (Fig. 2). Porewater Fe concentrations exhibit a similar trend to Mn, with a pronounced peak of 700 µmol/L at a depth of 12–15 cm. Beneath this, porewater Fe decreases, though remains high with a concentration around 400 µmol/L (Fig. 2). Porewater Zn displays a less pronounced variation, with an increase in porewaters compared to the overlying water column, and a broad maximum between 10 and 25 cm depth. Porewater phosphate displays a similar profile to that of Fe and Mn, with a broad peak between 10 and 30 cm depth of up to 50 µmol/L.

4.2. Sediment metal and organic carbon contents

All sediments analysed for metals exhibit a characteristic vertical distribution (Fig. 3). The upper 12 cm sediment contains a relatively constant concentration of metals (means of 1200 µg/g Mn, 550 µg/g Cu, 1500 µg/g Zn, 1000 µg/g Pb, and 40,000 µg/g Fe; Fig. 3). Below 12 cm in depth all metal concentrations show significant increases (Fig. 3). Between 12 and 17 cm concentrations of metals are up to an order of magnitude higher than in the sediment above. Within this part of the sediment column Zn concentrations reach 30,000 µg/g, Cu concentrations reach 7000 µg/g, Pb concentrations reach 4000 µg g^{-1}, Mn concentrations reach 2500 µg/g and Fe concentrations reach 150,000 µg/g (Fig. 3). Beneath this zone of enrichment metal concentrations in the sediment fall, displaying values that are the same, or lower than, the upper 12 cm. Total P in the sediment is between 3000 and 4000 µg/g, except for that depth characterised by high metal contents where total P concentrations are 2000 µg/g or less. Inorganic P ranged between 1000 and 3000 µg/g and was between 70% and 95% of the total P. Total organic carbon (TOC) contents in the sediment exhibit values of up to 10% in the upper layers, with a gradual decrease

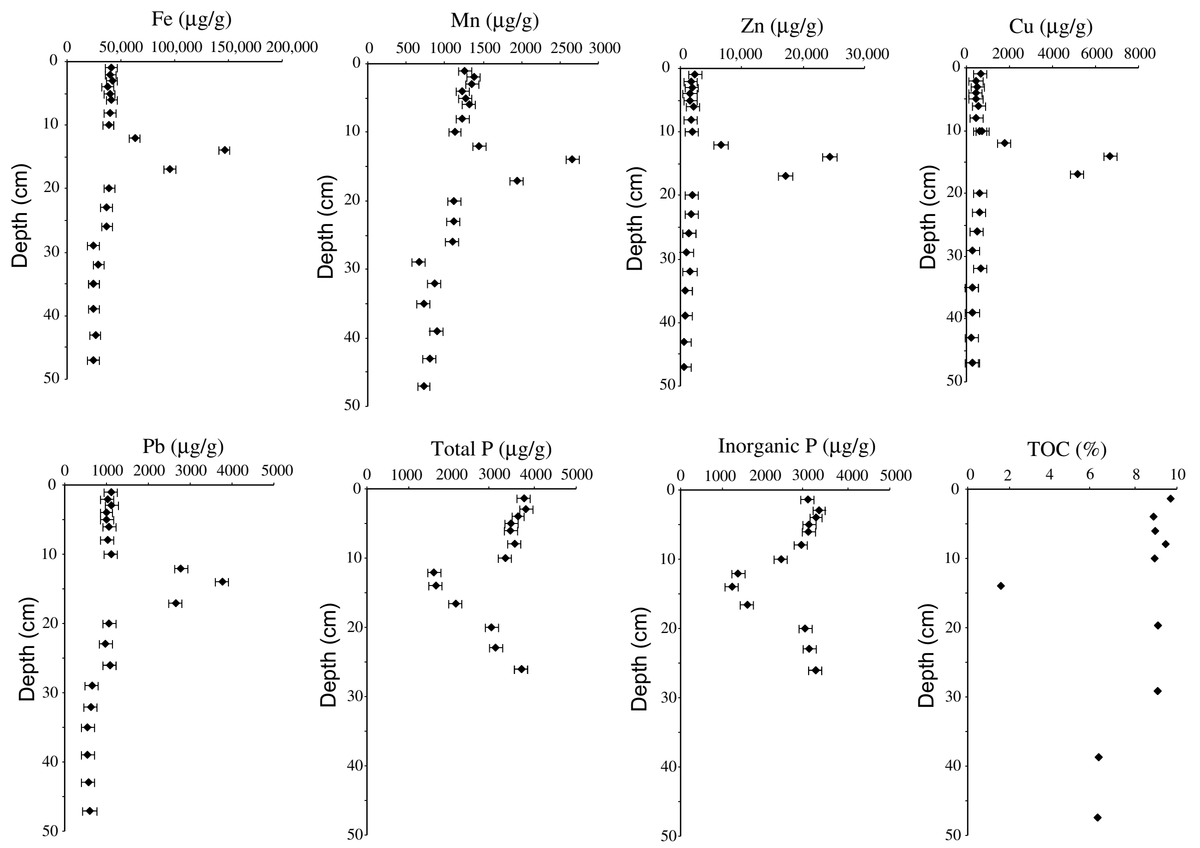

Fig. 3. Sediment concentrations of Fe, Zn, Cu, Mn, Pb, total P and inorganic P with depth for a typical Salford Quays sediment core. Depths indicated are metres below the sediment–water interface (SWI). Note the marked increase in metals in concentrations at depths between 12 and 17 cm. Error bars are based on the standard error for the data set (triplicate analyses).

to 6.5% with depth. The layer in the sediment characterised by high metal contents contains low TOC (<2%).

4.3. Detrital grain mineralogy

Throughout the sediment column the detrital mineralogy of the sediment is composed predominantly of quartz grains, clays, and anthropogenic grains (metal-rich fragments and glasses). However, there are systematic patterns in the distribution of these grains in the sediment column. The upper 12 cm of the sediment is composed predominantly of fine-grained quartz and clay material, with abundant diatoms. Anthropogenic grains were not observed in the upper 12 cm. Beneath 12 cm depth in the sediment column, the detrital mineralogy of the sediments is significantly more variable, with silt and sand-sized quartz grains and a heterogenous mix of anthropogenic grains. Whilst anthropogenic grains are present throughout the sediment column beneath 12 cm, they are most abundant at 12–17 cm depth (based on SEM observations). At this depth there is an abundance of Fe- and metal-rich glass grains (Fig. 4). These glass grains range in size from 100 µm to 2 mm and are varied in their mineralogy. Most fall into one of two classes, Fe-rich and Fe-poor glasses. The Fe-rich glass grains are composed of a glass matrix, with inclusions of metal-rich blebs and dark crystalline areas (Fig. 4a–d). Typical total analyses of these grains are shown in Tables 1 and 2. These glasses are alumino-silicate glasses containing variable amounts of Ca, Mg, Na and K. The Fe-rich glass contains high concentrations of Fe (average of 38.5% FeO) and Zn (8.3% ZnO), with significant amounts of Pb, Ni and Sn (Table 1). The dark inclusions are high in Cr (up to 19.5% Cr_2O_3), and Al (average 39.5% Al_2O_3) with low amounts of Si (Table 1). The metallic blebs within the glasses are up to 20 µm across and are dominated by Cu, with

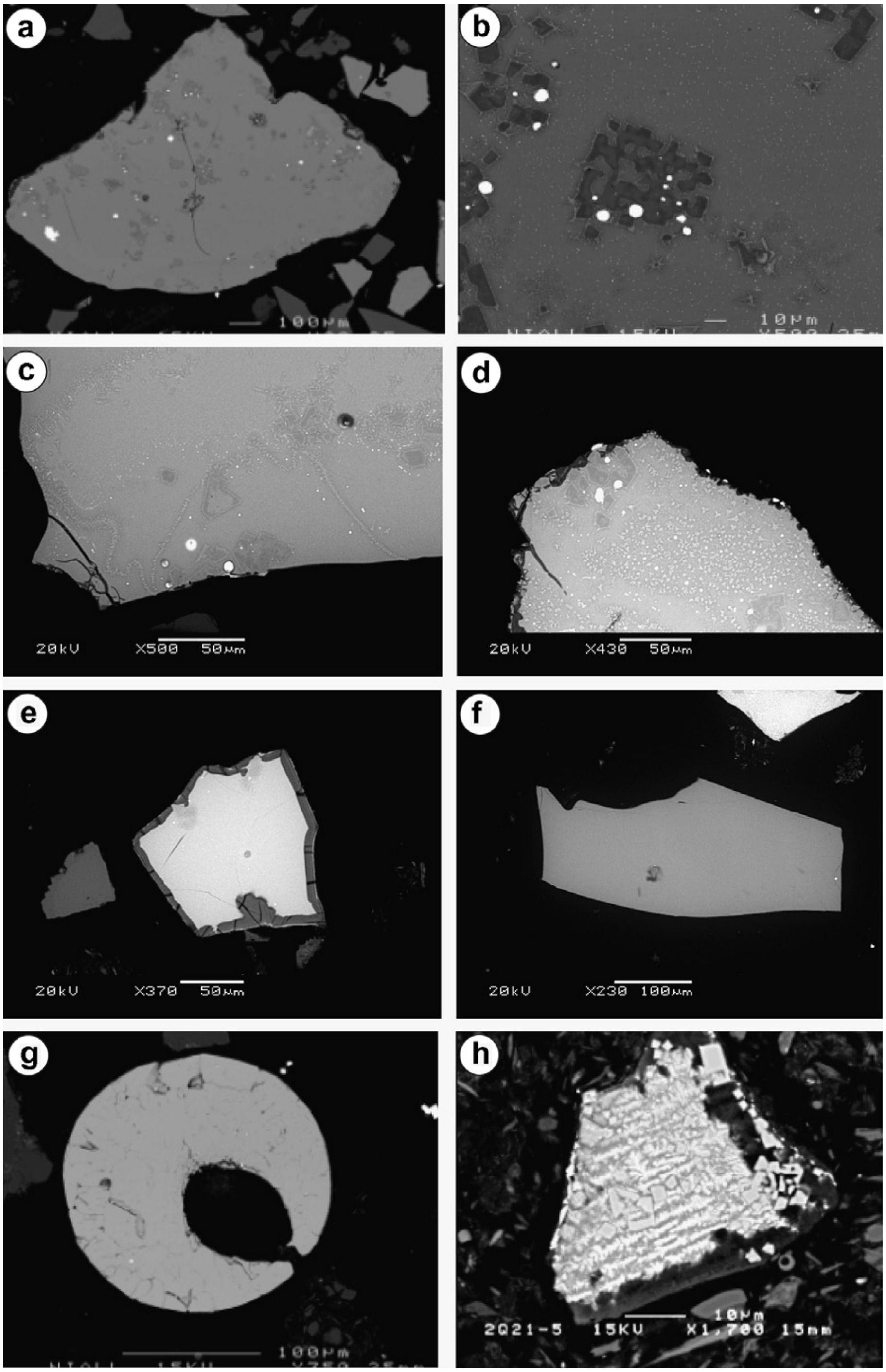

Fig. 4. Backscattered electron (BSE) images of anthropogenic glass grains within Salford Quays sediments. (a–d) Iron-rich furnace-derived glass grains from between 12 and 17 cm depth in the sediment. Bright areas within the glasses are Cu-rich metallic inclusions. Dark areas are Cr- and Al-rich. (e) Spherule of glass. (f) Metal-rich detrital grain within sediment beneath 17 cm. Scale bars are shown for each micrograph.

significant Sn, Ni and Pb (Table 2). The low S contents indicate that the inclusions are of elemental metals rather than metal sulfides. Glass grains may also exhibit chemical zonation (Fig. 4e). Iron-poor glasses contain significantly less Fe (average 9.15% FeO) and low concentrations of other metals (Table

Table 1
Elemental composition of glass grains in the Salford Quays sediment, determined by electron microprobe analysis

	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	MgO	CaO	MnO	FeO	NiO	CuO	ZnO	SnO	PbO	Na_2O	K_2O	Total
Fe-rich glasses	28.15	0.26	7.14	0.07	4.77	5.87	0.70	31.08	0.53	1.75	14.60	0.51	1.16	0.94	0.37	97.93
	27.90	0.26	7.17	0.01	4.86	5.88	0.68	31.81	0.59	2.10	14.69	0.55	1.11	0.84	0.37	98.87
	25.10	0.25	7.83	0.04	4.97	2.91	0.73	43.42	0.78	0.79	8.85	0.71	1.14	0.69	0.34	98.57
	28.25	0.37	8.88	0.17	4.97	7.43	1.00	36.68	0.23	1.86	6.40	0.20	0.36	0.92	0.39	98.19
	26.84	0.30	7.98	0.08	5.33	6.79	0.71	43.00	0.20	0.63	5.07	0.18	0.32	0.43	0.36	98.25
	27.10	0.30	6.14	0.02	5.32	4.12	0.52	37.72	0.54	1.43	10.52	1.02	1.89	1.10	0.36	98.10
	23.92	0.27	6.80	0.09	6.49	5.66	0.79	47.08	0.28	0.77	4.84	0.18	0.36	0.61	0.33	98.47
	31.20	0.35	9.06	0.05	4.78	10.24	0.57	32.22	0.45	0.57	6.62	0.38	0.71	0.56	0.39	98.16
	31.10	0.34	8.86	0.02	4.73	10.18	0.63	31.94	0.46	0.66	6.60	0.38	0.65	0.49	0.39	97.44
	28.94	0.29	8.17	0.02	5.03	7.57	0.74	33.59	0.40	1.12	9.90	0.42	0.75	0.68	0.42	98.07
	20.40	0.53	9.53	0.08	4.60	4.86	0.57	44.47	1.06	0.26	9.24	0.40	0.42	0.64	0.31	97.37
	30.23	0.29	7.23	0.03	4.94	5.38	0.70	35.33	0.45	1.14	8.07	0.74	1.58	0.74	0.43	97.29
	25.56	0.34	7.80	0.02	5.23	5.31	0.92	44.15	0.22	0.39	6.01	0.20	0.44	0.76	0.41	97.79
	25.33	0.36	7.90	0.03	5.14	5.37	0.94	44.33	0.15	0.22	6.09	0.19	0.42	0.70	0.39	97.62
	27.52	0.36	8.42	0.03	5.22	5.39	1.02	40.97	0.07	0.22	6.66	0.21	0.47	0.60	0.33	97.55
Average ($n = 15$)	27.17	0.32	7.93	0.05	5.09	6.20	0.75	38.52	0.43	0.93	8.30	0.42	0.79	0.71	0.37	97.98
SD	2.75	0.07	0.90	0.04	0.43	1.93	0.15	5.45	0.25	0.60	2.99	0.24	0.47	0.17	0.03	0.45
Dark inclusions In Fe-rich glasses	6.60	0.20	32.37	7.69	4.10	1.26	0.28	22.21	1.26	0.52	22.15	0.13	0.22	0.78	0.06	99.82
	0.22	0.24	34.13	13.50	4.92	0.04	0.13	25.21	1.81	0.06	17.39	0.12	0.01	0.51	0.00	98.29
	0.08	0.11	45.80	9.71	3.40	0.00	0.34	20.38	0.20	0.05	18.74	0.01	0.00	0.57	0.00	99.41
	0.08	0.12	37.70	19.52	6.49	0.00	0.28	19.90	0.57	0.10	14.45	0.00	0.00	0.44	0.00	99.67
	2.99	0.14	42.42	6.86	5.50	0.35	0.30	23.92	0.51	0.06	15.41	0.02	0.07	0.62	0.03	99.20
	2.03	0.29	45.07	3.94	7.81	0.58	0.39	26.78	0.41	0.17	10.00	0.04	0.03	0.32	0.02	97.90
Average ($n = 6$)	2.00	0.18	39.58	10.20	5.37	0.37	0.29	23.07	0.79	0.16	16.36	0.06	0.06	0.54	0.02	99.05
SD	2.33	0.07	5.20	5.07	1.47	0.45	0.08	2.49	0.56	0.16	3.77	0.05	0.07	0.14	0.02	0.71
Fe-poor glasses	49.41	1.33	29.72	0.06	3.21	4.88	0.08	5.58	0.02	0.07	0.04	0.00	0.01	0.64	4.09	99.38
	47.44	0.94	26.88	0.03	1.85	7.22	0.12	10.07	0.01	0.03	0.00	0.00	0.03	0.68	2.68	97.98
	46.58	0.98	26.40	0.02	2.24	2.80	0.18	12.44	0.02	0.04	0.05	0.01	0.05	1.49	3.40	96.74
	42.99	0.98	24.36	0.03	2.36	10.94	0.18	10.68	0.03	0.03	0.00	0.00	0.01	0.93	2.97	96.50
	43.75	0.86	23.67	0.02	2.23	11.02	0.13	11.31	0.01	0.04	0.04	0.00	0.00	0.66	3.01	96.78
	45.47	1.07	28.44	0.04	2.04	3.88	0.12	10.56	0.04	0.07	0.07	0.01	0.01	1.24	3.22	96.30
	49.67	1.25	31.72	0.05	2.04	3.52	0.12	3.36	0.00	0.00	0.03	0.00	0.00	1.55	4.01	97.36
	44.70	1.09	27.17	0.04	1.78	8.38	0.12	8.64	0.04	0.07	0.12	0.00	0.07	1.02	3.26	96.49
	44.95	1.00	25.02	0.03	2.07	9.89	0.13	9.26	0.04	0.02	0.16	0.00	0.02	0.90	3.13	96.63
	44.76	0.89	23.82	0.01	2.19	11.13	0.14	9.63	0.03	0.02	0.02	0.00	0.00	0.66	3.18	96.53
Average ($n = 10$)	45.97	1.04	26.72	0.03	2.20	7.37	0.13	9.15	0.02	0.04	0.05	0.00	0.02	0.98	3.29	97.01
SD	2.15	0.14	2.52	0.01	0.38	3.19	0.03	2.60	0.01	0.02	0.05	0.01	0.02	0.33	0.42	0.90

Oxide totals of less than 100% most likely indicates the presence of water in the structure, which was not analysed for, or the presence of Fe_2O_3 as well as FeO.

Table 2
Mean compositions (with standard deviations in brackets) of metallic inclusions within Fe-rich glass grains as determined by electron microprobe analysis ($n = 4$)

Element	Weight%
Cr	0.06 (0.10)
Cu	69.55 (6.66)
Fe	5.22 (5.22)
Mn	0.08 (0.04)
Ni	9.53 (3.72)
Pb	2.02 (0.39)
S	0.44 (0.32)
Sn	7.75 (2.32)
Zn	1.07 (0.37)
Total	95.72 (5.91)

The presence of a total weight% of less than 100% suggests the presence of other elements, or O, which were not determined.

1), and lack inclusions or zonation (Fig. 4f). These Fe-poor glass grains may also be spherical, ranging in size from 10 μm to 150 μm (Fig. 4g). Whilst these glass grains are concentrated in a zone 12–17 cm in depth in the sediment, similar anthropogenic grains are evident at greater depths (Fig. 4h). Based on SEM observations no grainsize variations in the matrix were observed, except for an increase in coarser metal-rich grains between 12 and 17 cm.

The outer edges of the Fe-rich glass grains show clear evidence for chemical dissolution (Fig. 5). Both pitting textures on the outer surfaces of the grains (Fig. 5a) and grain-scale dissolution of glasses (Fig. 5b) can be observed. In many cases, heterogeneity in chemical composition has led to heterogeneous dissolution (Fig. 5b).

4.4. Authigenic mineralogy

The presence of the iron phosphate vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) was observed in the X-ray diffraction traces of sediment samples (Fig. 6). Vivianite was present in samples throughout the sediment column, but displayed a larger X-ray diffraction peak in deeper sediment samples, suggesting greater amounts

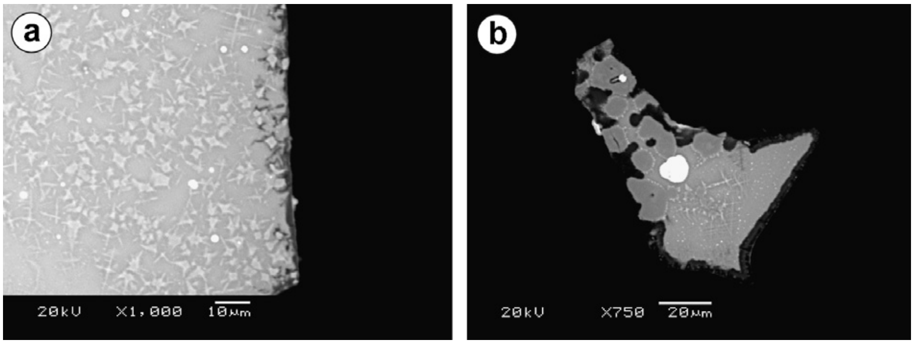

Fig. 5. Backscattered electron (BSE) images showing evidence for dissolution of anthropogenic glass grains. (a) Details of edge of Fe-rich glass grains showing dissolution features, resulting in pitted surface. Scale bar = 10 μm. (b) Iron-rich glass grain showing preferential dissolution of more Fe-rich (slightly brighter) areas of the glass. Scale bar = 20 μm.

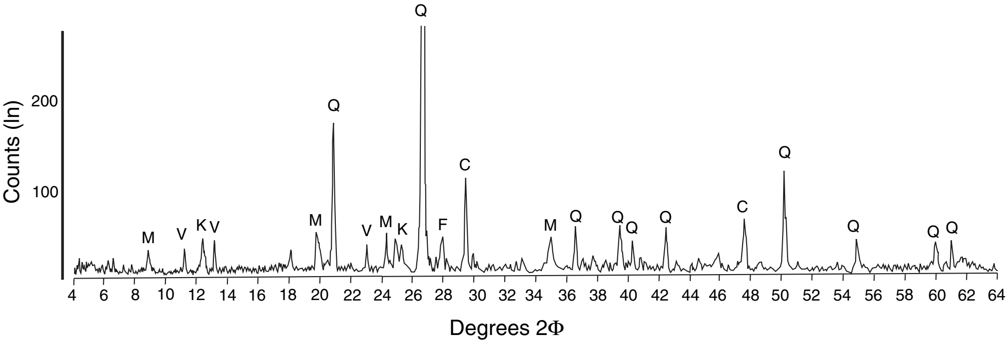

Fig. 6. X-ray diffraction trace from sediment sample at depth 10 cm in the Salford Quays, confirming the presence of vivianite (V, vivianite; M, muscovite; K, kaolinite; Q, quartz; C, calcite; F, feldspar).

at depth. No quantitative measures of vivianite were made, but the presence of significant X-ray diffraction peaks suggests that levels in the sediment are in excess of 1%. Backscatter electron imaging shows this mineral to take the form of radiating lath-shaped crystals and needle-like masses growing within the sediment matrix (Fig. 7). Typical elemental analyses of these vivianite grains are shown in Table 3. There is significant Mn concentrations in the vivianite crystals (up to 5.4% MnO). In addition to Mn, significant concentrations of Zn (up to 550 μg/g), Cu (up to 520 μg/g) and Pb (up to 700 μg/g) are also present (Table 3). Also observed in backscattered electron images is authigenic pyrite, taking the form of framboidal pyrite. Based on visual observations pyrite is under 10% of the number of grains of vivianite. No pyrite or Fe monosulfides were observed in X-ray diffraction traces, suggesting that these minerals are present in only trace amounts. Electron microprobe analyses of framboidal pyrite show it to contain insignificant concentrations of Pb and Zn, but having Cu concentrations of up to 900 μg/g.

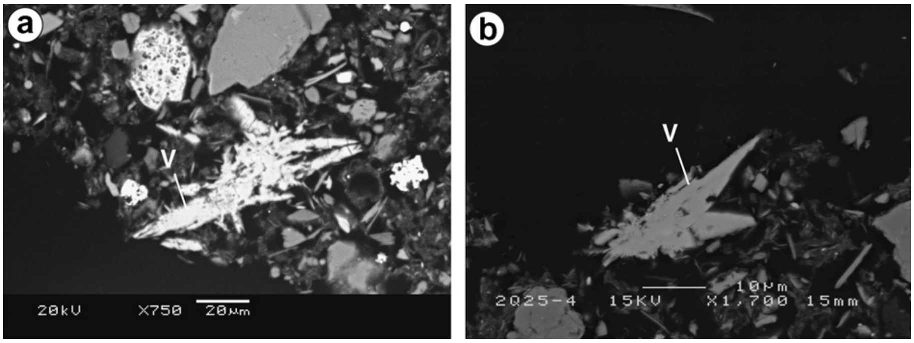

Fig. 7. (a, b) Backscattered electron (BSE) images of authigenic vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) within Salford Quays sediments. The vivianite (V) takes the forms of radiating needles and laths. Scale bars are shown for each micrograph.

Table 3
Major and trace element data for authigenic vivianite in Salford Quays sediments, determined by electron microprobe analysis

	FeO	P_2O_5	CaO	MgO	MnO	Total	Zn	Cu	Pb
Individual vivianite crystals	44.68	31.90	0.62	0.18	1.97	79.35	–	147	234
	45.71	30.84	0.42	0.17	1.78	78.92	–	–	
	45.35	30.71	0.39	0.11	1.44	78.00	217	–	
	42.74	32.83	0.80	0.50	4.24	81.11	–	–	157
	44.81	31.88	0.90	0.33	2.46	80.38	–	–	–
	44.17	31.48	0.69	0.26	2.85	79.45	–	–	480
	44.57	31.59	0.63	0.09	2.22	79.10	–	–	–
	41.01	28.89	0.73	0.27	5.36	76.26	350	240	350
	44.03	31.43	0.90	0.43	2.93	79.72	100	–	300
	44.15	33.72	1.05	1.07	1.44	81.43	–	160	140
	43.77	30.57	0.73	0.29	2.09	77.45	315	–	180
	42.37	30.97	0.83	0.30	3.30	77.77	251	–	270
	37.80	29.91	0.67	0.24	2.04	70.65	320	520	700
	45.59	32.72	0.23	0.11	2.09	80.74	180	–	250
	42.31	33.77	0.87	0.49	4.25	81.69	–	–	100
	42.07	29.29	0.26	0.15	3.60	75.37	–	–	250
	42.99	34.17	1.47	0.57	2.92	82.11	–	–	–
	38.12	29.86	0.54	0.14	3.82	72.47	550	100	110
	45.91	33.69	0.33	0.06	2.36	82.36	–	–	–
Average ($n = 19$)	43.27	31.59	0.69	0.30	2.80	78.65			
SD	2.26	1.53	0.29	0.23	1.04	3.08			

Major elements are quoted in weight% oxide. Zn, Cu and Pb are quoted in μg/g. Where no figure is quoted the concentration was below the detection limit. The low value for total oxides (mean of 78.65%) is a result of the presence of structural water in vivianite, which was not determined.

5. Discussion

5.1. Detrital mineralogy and geochemistry

Since water quality remediation and hydrological isolation the sediment in the Quays has been dominated by atmospheric and autochthonous deposition, and this has resulted in the predominance of fine-grained quartz and clay grains, and siliceous diatoms in the upper parts of the sediment column. Whilst these upper sediments are characterised by lower metal contents than deeper in the sediment cores, the concentrations of Cu, Zn and Pb are comparable to contemporaneous contaminated urban sediments elsewhere in Manchester (Robertson et al., 2003). Between 12 and 17 cm depth in the sediment, metal-rich glass grains are present (Fig. 5), explaining the high metal concentrations in the sediment at this depth. Such grains are most likely the result of furnace-derived slag from Fe and Cr steel production. This is consistent with their composition of Fe–Ca–Si glass and Cu, Zn, Cr- and Ni-rich inclusions (Lind et al., 2001). Similar grains have been described from both contaminated soils (Gee et al., 1997; Parsons et al., 2001; Lottermoser, 2002) and anthropogenically impacted sediments (Pirrie et al., 1997; Rees et al., 1998). These grains, therefore, represent a detrital phase quite distinct from natural sediments. These grains are most likely present in an enrichment layer as a result of the input of material into the Quays during the initial stages of site remediation and clearance (Taylor et al., 2003). Sediments below 17 cm in depth are predominantly composed of a mix of detrital quartz, clays and frequent anthropogenic grains, likely sourced from riverine and industrial inputs into the Quays when they were connected to the MSC.

Estimated total P through the sediment column exhibits a maximum of 4000 μg/g. These concentrations are higher than typical fine-grained suspended sediment from river basins (500–2000 μg/g) but are typical of the concentrations found in urbanised river basins (up to 6000 μg/g; Owens and Walling, 2002). The source for the high concentrations of total P found in the Salford Quays is probably urban-derived organic matter. However, the inorganic P fraction accounts for 70–95% of the total P. As no detailed P speciation data are available it is not clear what proportion of this inorganic P is present as Fe-oxide bound, apatite or vivianite fractions. The upper 5 cm of the sediment contains a lower proportion of inorganic P, suggesting that P is rapidly cycled from organic to inorganic forms during the earliest phases of diagenesis (e.g. Hupfer et al., 1995; Gonsiorczyk et al., 2001).

5.2. Porewaters

The decreases in porewater SO_4 and NO_3 indicate the activity of bacterial SO_4 reduction and NO_3 reduction both important early diagenetic processes in aquatic sediments (e.g., Mackin and Swider, 1989; Canfield et al., 1993; Blackburn and Blackburn, 1993). Although O_2 and redox potential were not measured in the porewaters, the presence of SO_4 and NO_3 reduction at such shallow depths indicate that O_2 is depleted in the sediments almost immediately, and hence the redoxcline is situated almost directly beneath the sediment–water interface. The release of NH_4 into the porewater is consistent with bacterial organic matter oxidation, as NH_4 is a product of the breakdown of organic matter (Burdige, 1991).

The presence of Mn and Fe in porewaters indicates that within the sediment Fe and Mn are being released from the solid phase into solution. Such porewater Mn and Fe are commonly documented for organic-rich aquatic sediments and are usually attributed to bacterial reduction of Fe(III) oxides ($2Fe_2O_3 + CH_2O + 6H^+ \rightarrow 4Fe^{2+} + CO_3^{2-} + 4H_2O$) and Mn(IV) reduction ($2MnO_2 + CH_2O + 2H^+ \rightarrow 2Mn^{2+} + CO_3^{2-} + 2H_2O$) (Lovley, 1991; Burdige, 1993; Coleman et al., 1993). Within such sediments, a peak in Mn porewater concentration is generally observed close to the surface, followed by a broader peak in porewater Fe. This is because the reduction of Mn oxides is thermodynamically favoured over the reduction of Fe oxides (Froelich et al., 1979; Coleman, 1985), and because Fe(II) can abiotically reduce Mn(IV) (Burdige, 1993). Furthermore, it has been recognised that Fe(III) oxides possess a range of reactivities (Canfield et al., 1992; Postma, 1993) that result in a range of susceptibility to dissimilatory Fe(III) reducing bacteria (Roden and Wetzel, 2002). This results in Fe(III) reduction taking place through a wide range of burial depths within sediments. Concentrations of other metals have also been shown to peak in sediment porewaters, and this is usually ascribed to the release of metals adsorbed onto Fe and Mn oxides during Mn and Fe reduction (Hamilton-Taylor et al., 1996a,b). The release of P into porewaters has similarly been ascribed to the reductive dissolution of

Fe(III) oxides, the surfaces of which P adsorbs to in freshwater sediments (Hupfer et al., 1995; Gonsiorczyk et al., 2001).

In the case of the Salford Quays sediment the Mn, Fe and Zn porewater peaks are coincident, and are at the same depth as the layer of metal enrichment. This strongly suggests that the composition of the sediment at that depth is having a control on the distribution of porewater Mn, Fe and Zn. As noted above, the sediment at a depth of 12–17 cm is composed of a high volume of metal-rich silica glasses. This, therefore, leads to the possibility that chemical dissolution of these glasses has led to the release of Mn, Fe and Zn into the porewaters. There is clear evidence for dissolution of these glasses (Fig. 6).

From the study of contaminated soils, furnace-derived glasses are known to be prone to weathering dissolution, with the consequential release of contaminants (Gee et al., 1997, 2001; Parsons et al., 2001; Lottermoser, 2002). Dissolution of both natural and synthetic glasses is strongly pH-dependent, with markedly higher dissolution rates at low pH (Woodley and Walters, 1986; Parsons et al., 2001; Gislason and Oelkers, 2003). Similar dissolution studies have not been undertaken for aquatic sediments, and the role of Eh is also undetermined. However, organic-acid generation during early diagenesis of freshwater organic-rich sediments has been clearly documented (McMahon et al., 1992; Chapelle and Bradley, 1996; Manning, 1997; Manning and Bewsher, 1997). Such acid generation is likely to impact upon glass solubility and could explain the observed dissolution in the organic-rich Salford Quays sediments.

5.3. Authigenic mineral precipitation

The presence of authigenic vivianite ($Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$) has been commonly noted within organic-rich lake sediments (Nriagu and Dell, 1974; Emerson, 1976; Brooks and Eddington, 1994; Deike et al., 1997; Fagel et al., 2005), and also in organic-rich anthropogenic sediments (Goslar et al., 1999; Dodd et al., 2000). It has long been known that vivianite plays a role in the cycling of P in lake systems (e.g. Mortimer, 1941). Vivianite has been shown to be stable under reducing conditions and high Fe^{2+} and PO_4^{2-} activities, and low sulphide activities (Rosenquist, 1970; Nriagu, 1972; Emerson and Widmer, 1978). In most studies the source of Fe^{2+} is ascribed to the reduction of Fe(III) oxides, and this reaction has also been proposed to release P adsorbed onto the Fe(III) oxides. Recently, Hyacinthe and Van Cappellen (2004) have documented the formation of a ferric-phosphate in freshwater sediments, but in the Salford Quays direct determination by electron microprobe has confirmed the stochiometry of the grains as vivianite, as well as confirmation by X-ray diffraction.

Electron microprobe data indicate that the vivianite grains contain moderate levels of the trace metals Mn, Pb, Cu and Zn. Manganese displays by far the highest values in the vivianite, reflecting the high levels of Mn in the sediment porewaters. Nriagu and Dell (1974) showed that the most stable form of vivianite in natural sediments is a solid state solution with redlingite ($Mn_3^{2+}(PO_4)_2 \cdot 8H_2O$). However, there is no direct evidence for the presence of redlingite, either through X-ray diffraction or electron microscopic analysis. Therefore, it is not possible to determine whether redlingite/vivianite or Mn-substituted vivianite is present. Very little information on trace element uptake into vivianite is available. Fagel et al. (2005) report concentrations of Zn, Cu and Pb up to 195, 167 and 40 ppm, respectively. In the Salford Quays sediments Zn, Pb and Cu concentrations in the vivianite are variable, but reach a maximum of 550, 520 and 700 μg/g, respectively, suggesting that vivianite acts as a sink for these metals in this sediment. Vivianite has also been proposed to be a sink for As in groundwater systems (Horneman et al., 2004).

The presence of minor pyrite within the Salford Quays sediments indicates that although only minor SO_4 reduction is taking place, there is sufficient to lead to pyrite precipitation. Trace element analysis indicates that Cu has been taken up by the pyrite. Iron sulphides are known to act as sinks for metals within marine sediments (Cooper and Morse, 1998, 1999), but the nature of this trace metal association with Fe sulphide has been less well established. Many studies have suggested that metals form surface-adsorbed complexes with Fe sulphides. However, Cu has been observed to be precipitated within pyrite in contaminated estuarine sediments in the form of CuS_2 (e.g.. Parkman et al., 1996). Whilst the data set of pyrite composition in this present study is very limited, it is consistent with these observations.

6. Implications

This study has implications for both the analysis of metal diagenesis in sediments, and in the risk assessment of contaminated sediments. Firstly, the observation that chemical dissolution of anthropogenic grains (metal-rich glasses) may be an important mechanism for metal release in contaminated sediments means that in such sediments both chemical dissolution and bacterial Fe and Mn reduction needs to be quantified in mass balance and flux models. Secondly, the observation that vivianite is an important authigenic phase in organic-rich freshwater sediments may have implications for assessment and long-term risk models. It has been established that in marine and brackish sediments the precipitation of Fe sulfides, via bacterial SO_4 reduction, leads to the uptake of metals in metal sulfides (Morse and Luther, 1999) and has been used to form the basis for sediment quality criteria (Ankley et al., 1996). The absence of SO_4 in freshwater has been assumed to result in more mobile, bioavailable metals in these sediments (Ankley et al., 1996). It has been shown here that vivianite precipitated in freshwater sediments can also take-up trace metals, although the levels observed in this study are not high (up to 700 ppm). Therefore, more study should be undertaken on the capacity of such vivianite to take-up trace metals in contaminated sediments. It should be noted that vivianite will only act as a sink for trace metals under continuing reducing conditions; sediment re-suspension and re-oxidation of vivianite will lead to release of these metals back into the aquatic system in a similar manner to Fe sulfide-bound metals (Stephens et al., 2001).

7. Conclusions

1. Contaminated freshwater sediments deposited in the Salford Quays, Greater Manchester, UK, contain a mix of natural and anthropogenic detrital grains. The latter, in the form of metal-rich glass grains, contain high concentrations of Zn, Cu, Pb and Cr and are particularly enriched at a depth of 12–17 cm in the sediment as a result of historical inputs. As a result, metal concentrations in the sediment are high. Phosphorus concentrations are also high in the sediment, as a result of high organic-matter input.
2. Sediment porewaters contain significant concentrations of Fe, Mn, Zn and phosphate. Petrographic observations indicate that the metal-rich glass grains are undergoing chemical dissolution during early diagenesis, supplying Fe and Zn to porewaters. Bacterial Fe(III) and Mn(IV) reduction is also likely to supply Fe^{2+} and Mn^{2+} to porewaters, with phosphate released from Fe oxide reduction or organic matter oxidation.
3. Authigenic vivianite $(Fe_3^{2+}(PO_4)_2 \cdot 8H_2O)$ is abundant within the sediment and contains a significant amount of Mn, either in the form of redlingite $(Mn_3^{2+}(PO_4)_2 \cdot 8H_2O)$ or Mn-substituted vivianite. Significant amounts of Zn, Cu and Pb have been taken-up into this vivianite, suggesting that it acts as a long-term sink for these metals in this sediment.

Acknowledgements

This work was funded through a NERC Grant (No. GST/02/2255), as part of the URGENT programme, which is gratefully acknowledged. Access to the Cameca 100SX electron microprobe at the University of Manchester was provided through the NERC external user facility, and Dave Plant is thanked for assistance in this. Ulle Tillman, Alastair Bewsher, David McKendrick, Dave Groom and Paul Lythgoe are thanked for technical assistance. Review comments from Karen Hudson-Edwards and an anonymous reviewer significantly improved this manuscript.

References

Ankley, G.T., Di Toro, D.M., Hansen, D.J., Berry, W.J., 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environ. Toxicol. Chem. 15, 2056–2066.

Aspila, K.I., Agemian, H., Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101, 187–197.

Blackburn, T.H., Blackburn, N.D., 1993. Rates of microbial processes in sediments. Philos. Trans. Roy. Soc. Lond. A 344, 49–58.

Boult, S., Hendry, K., 1995. Gas generation in the Manchester Ship Canal. Open University Geol. Soc. J. 16, 1–5.

Bromhead, J.C., Beckwith, P., 1994. Environmental dredging on the Birmingham Canals: water quality and sediment treatment. J. Inst. Water Environ. Manag. 8, 350–359.

Brooks, A.S., Eddington, D.N., 1994. Biogeochemical control of phosphorus cycling and primary production in Lake Michigan. Limnol. Oceanogr. 39, 961–968.

Bryant, C.L., Farmer, J.G., MacKenzie, A.B., Bailey-Watts, A.E., Kirika, A., 1997. Manganese behaviour in the sediments of diverse Scottish freshwater lochs. Limnol. Oceanogr. 42, 918–929.

Burdige, D.J., 1991. The kinetics of organic matter mineralization in anoxic marine sediments. J. Mar. Res. 49, 727–761.

Burdige, D.J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. Earth Sci. Rev. 35, 249–284.

Callender, E., Van Metre, P.C., 1997. Reservoir sediment cores show U.S. lead declines. Environ. Sci. Technol. 31, 424A–428A.

Canfield, D.E., Raiswell, R., Bottrell, S., 1992. The reactivity of sedimentary iron minerals towards sulphide. Am. J. Sci. 292, 659–683.

Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochim. Cosmochim. Acta 57, 3867–3883.

Carignan, R., Flett, R.J., 1981. Post-depositional mobility of phosphorus in lake-sediments. Limnol. Oceanogr. 26, 361–366.

Chapelle, E.H., Bradley, P.M., 1996. Microbial acetogenesis as a source of organic acids in ancient Atlantic Coastal Plain sediments. Geology 24, 925–928.

Charlesworth, S.M., Foster, I.D.L., 1999. Sediment budgets and metal fluxes in two contrasting urban lake catchments, Coventry, UK. Appl. Geogr. 19, 199–210.

Coleman, M.L., 1985. Geochemistry of diagenetic non-silicate minerals: kinetic considerations. Philos. Trans. Roy. Soc. Lond. A 315, 39–56.

Coleman, M.L., Hedfick, D.B., Lovley, D.R., White, D.C., Pye, K., 1993. Reduction of Fe(III) in sediments by sulphate-reducing bacteria. Nature 361, 436–438.

Cooper, D.C., Morse, J.W., 1998. Extractability of metal sulfide minerals in acidic solutions: applications to environmental studies of trace metal contamination within anoxic sediments. Environ. Sci. Technol. 32, 1076–1078.

Cooper, D.C., Morse, J.W., 1999. Selective extraction chemistry of toxic metal sulfides from sediments. Aquat. Geochem. 5, 87–97.

Covelli, S., Faganeli, J., Horvart, M., Brambati, A., 1999. Porewater distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). Estuar. Coast. Shelf Sci. 48, 415–428.

Deike, R.G., Granina, L., Callender, E., McGee, J.J., 1997. Formation of ferric iron crusts in Quaternary sediments of Lake Baikal, Russia, and implications for palaeoclimate. Mar. Geol. 139, 21–46.

Dodd, J., Large, D.J., Fortey, N.J., Milodowski, A.E., Kemp, S., 2000. A petrographic investigation of two sequential extraction techniques applied to anaerobic canal bed mud. Environ. Geochem. Health 22, 281–296.

Emerson, S., 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochim. Cosmochim. Acta 40, 925–934.

Emerson, S., Widmer, G., 1978. Early diagenesis in anaerobic lake sediments – II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. Geochim. Cosmochim. Acta 42, 1307–1316.

Fagel, N., Alleman, L.Y., Granina, L., Hatert, F., Thamo-Bozso, E., Cloots, R., Andre, L., 2005. Vivianite formation and distribution in Lake Baikal sediments. Global Planet. Change 46, 315–336.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090.

Gee, C., Ramsey, M.H., Maskall, J., Thornton, I., 1997. Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead. J. Geochem. Explor. 58, 249–257.

Gee, C., Ramsey, M.H., Thornton, I., 2001. Buffering from secondary minerals as a migration limiting factor in lead polluted soils at historical mining sites. Appl. Geochem. 16, 1193–1199.

Gibbs, R.J., 1977. Transport phases of transition metals in the Amazon and Yukon rivers. Geol. Soc. Am. Bull. 88, 829–843.

Gill, G.A., Bloom, N.S., Cappellino, S., Driscoll, C.T., Dobbs, C., McShea, L., Mason, R., Rudd, J.W.M., 1999. Sediment-water fluxes of mercury in Lavaca Bay, Texas. Environ. Sci. Technol. 33, 663–669.

Gislason, S.T., Oelkers, E.H., 2003. Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. Geochim. Cosmochim. Acta 67, 3817–3832.

Gonsiorczyk, T., Casper, P., Koschel, R., 2001. Mechanisms of phosphorus release from the bottom sediment of the oligotrophic Lake Stechlin: importance of the permanently oxic sediment surface. Arch. Hydrobiol. 151, 203–219.

Goslar, T., Ralska-Jasiewiczowa, M., Van Geel, B., Lacka, B., Szeroczynska, K., Chrost, L., Walanus, A., 1999. Anthropogenic changes in the sediment composition of Lake Gosciaz (central Poland) during the last 330 years. J. Paleolimnol. 22, 171–185.

Hamilton-Taylor, J., Davison, W., Morfett, K., 1996a. The biogeochemical cycling of Zn, Cu, Fe, Mn and dissolved organic C in a seasonally anoxic lake. Limnol. Oceanogr. 41, 408–418.

Hamilton-Taylor, J., Davison, W., Morfett, K., 1996b. A laboratory study of the biogeochemical cycling of Fe, Mn, Zn and Cu across the sediment–water interface of a productive lake. Aquat. Sci. 58, 191–209.

Horneman, A., Van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Connell, S., Hoque, M.A., Aziz, Z., Shamsudduha, M., Seddique, A.A., Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part 1. Evidence from sediment profiles. Geochim. Cosmochim. Acta 68, 3459–3473.

Horowitz, A.J., Elrick, K.A., Cook, R.B., 1993. Effect of mining and related activities on the sediment trace element geochemistry of Lake Coeur d'Alene, Idaho, USA. Part I: surface sediments. Hydrol. Proc. 7, 403–423.

Horowitz, A.J., Elrick, K.A., Robbins, J.A., Cook, R.B., 1995. Effect of mining and related activities on the sediment trace element geochemistry of Lake Coeur d'Alene, Idaho, USA. Part II: subsurface sediments. Hydrol. Proc. 9, 35–54.

Hu, W.F., Lo, W., Chau, H., Sin, S.N., Yu, P.H.F., 2001. Nutrient release and sediment oxygen demand in a eutrophic land-locked embayment in Hong Kong. Environ. Int. 26, 369–375.

Hudson-Edwards, K.A., Macklin, M.G., Taylor, M.P., 1999. 2000 years of sediment-borne heavy metal storage in the Yorkshire Ouse basin NE England, UK. Hydrol. Proc. 13, 1087–1102.

Hupfer, M., Gachter, R., Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat. Sci. 57, 305–324.

Hyacinthe, C., Van Cappellen, P., 2004. An authigenic iron phosphate phase in estuarine sediments: composition, formation and chemical reactivity. Mar. Chem. 91, 227–251.

Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron–phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. Hydrobiol. 235, 731–743.

Lind, B.B., Fallman, A.-M., Larsson, L.B., 2001. Environmental impact of ferrochrome slag in road construction. Waste Manag. 21, 255–264.

Lottermoser, B.G., 2002. Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia. Mineral. Mag. 66, 475–490.

Lovley, D.R., 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol. Rev. 55, 259–287.

Mackin, J.E., Swider, K.T., 1989. Organic matter decomposition pathways and oxygen consumption in coastal marine sediments. J. Mar. Res. 47, 681–716.

Macklin, M.G., 1996. Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. In: Anderson, M.G., Walling, D.E., Bates, P.D. (Eds.), Floodplain Processes. John Wiley and Sons, Chichester, pp. 441–460.

Manning, D.A.C., 1997. Acetate and propionate in landfill leachate: implications for recognition of microbiological influences on the composition of waters in sedimentary systems. Geology 25, 279–281.

Manning, D.A.C., Bewsher, A., 1997. Determination of anions in landfill leachates by ion chromatography. J. Chromatogr. A. 770, 203–210.

McMahon, P.B., Chapelle, E.H., Falls, W.F., Bradley, P.M., 1992. The role of microbial processes in linking sandstone diagenesis with organic-rich clays. J. Sediment. Petrol. 62, 1–10.

Morse, J.W., Luther, G.W., 1999. Chemical influences on trace metal–sulfide interactions in anoxic sediments. Geochim. Cosmochim. Acta 63, 3373–3378.

Mortimer, C.H., 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29, 280–329.

Nriagu, J.O., 1972. Stability of vivianite and ion pair formation in the system $Fe_3(PO_4)_2$–H_3PO_4–H_2O. Geochim. Cosmochim. Acta 36, 459–470.

Nriagu, J.O., Dell, C.I., 1974. Diagenetic formation of iron phosphates in recent lake sediments. Am. Mineral. 59, 934–946.

Owens, P.N., Walling, D.E., 2002. The phosphorus content of fluvial sediment in rural and industrialised river basins. Water Res. 36, 685–701.

Parkman, R.H., Curtis, C.D., Vaughan, D.J., Charnock, J.M., 1996. Metal fixation and mobilization in the sediments of Afon Goch Estuary, Dulas Bay, Anglesey. Appl. Geochem. 11, 203–210.

Parsons, M.B., Bird, D.K., Einaudi, M.T., Alpers, C.N., 2001. Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. Appl. Geochem. 16, 1567–1593.

Pirrie, D., Camm, G.S., Sear, L.G., Hughes, S.H., 1997. Mineralogical and geochemical signature of mine waste contamination, Tresillian River, Fal Estuary, Cornwall, UK. Environ. Geol. 29, 58–65.

Pirrie, D., Beer, A.J., Camm, G.S., 1999. Early diagenetic sulphide minerals in the Hayle Estuary, Cornwall. Geosc. Southwest England 9, 325–332.

Postma, D., 1993. The reactivity of iron oxides in sediments: a kinetic approach. Geochim. Cosmochim. Acta 57, 5027–5034.

Qu, W., Kelderman, P., 2001. Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: multivariate analysis for source tracing. Chemosphere 45, 919–925.

Rees, J.G., Ridgeway, J., Knox, R.W.O.B., Wiggans, G., Breward, N., 1998. Sediment-borne contaminants in rivers discharging into the Humber Estuary, UK. Mar. Poll. Bull. 37, 316–329.

Renberg, I., Wik Persson, M., Emeteryd, O., 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. Nature 368, 323–326.

Rivera-Duarte, I., Flegal, A.R., 1997. Pore-water silver concentrations and benthic fluxes from contaminated sediments of San Francisco Bay, California, U.S.A. Mar. Chem. 56, 15–26.

Robertson, D.J., Taylor, K.G., Hoon, S.R., 2003. Geochemical and mineral magnetic characterisation of urban sediment particulates, Manchester, UK. Appl. Geochem. 18, 269–282.

Roden, E.E., Wetzel, R.G., 2002. Kinetics of microbial Fe(III) oxide reduction in freshwater wetland sediments. Limnol. Oceanogr. 47, 198–211.

Rosenquist, I.Th., 1970. Formation of vivianite in Holocene clay sediments. Lithos 3, 327–334.

Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, New York.

Shine, J.P., Ika, R., Ford, T.E., 1998. Relationship between oxygen consumption and sediment-water fluxes of heavy metals in coastal sediments. Environ. Toxicol. Chem. 17, 2325–2337.

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. Environ. Poll. 114, 407–413.

Struthers, W.A.K., 1997. From Manchester Docks to Salford Quays: ten years of environmental improvements in the Mersey Basin Campaign. J. Ciwem 11, 1–7.

Taylor, K.G., Boyd, N.A., Boult, S., 2003. Sediments, porewaters and diagenesis in an urban water body, Salford, UK: impacts of remediation. Hydrol. Proc. 17, 2049–2061.

Trefry, J.H., Presley, B.J., 1976. Heavy metal transport from the Mississippi River to the Gulf of Mexico. In: Windom, H.L., Duce, R.A. (Eds.), Marine Pollution Transfer. Health Publications, Lexington, pp. 39–76.

White, K., Hendry, K., Bellinger, E.G., 1993. Ecological change as a consequence of water quality improvements at Salford Quays. In: White, K., Bellinger, E.G., Saul, M., Saul, A., Hendry, K. (Eds.), Urban Waterside Regeneration: Problems and Prospects. Ellis Horwood, Chichester, pp. 363–373.

Widerlund, A., 1996. Early diagenetic remobilisation of copper in near-shore marine sediments: a quantitative pore-water model. Mar. Chem. 54, 41–53.

Woodley, N.K.F., Walters, J.V., 1986. Hazardous waste characterisation extraction procedures for the analysis of blast-furnace slag from secondary lead smelters. Environ. Prog. 5, 12–17.