

Active sediment capping for pollutant mixtures: control of biogenic gas production under highly intermittent flows

Priscilla Viana, Ke Yin, Xiuhong Zhao and Karl Rockne

Abstract

Sediments in 'Bubbly Creek', located in the south fork of the south branch of the Chicago River (Illinois, USA) were characterized for the selection of amendments for an active capping demonstration project. Bubbly Creek is a 6800 ft (2000 m) creek that starts at the Racine Avenue pumping station (RAPS), the largest sewage pumping station in the world. During large storm events, the RAPS can discharge up to $6000 \text{ ft}^3 \text{ s}^{-1}$ ($175 \text{ m}^3 \text{ s}^{-1}$) of combined storm and wastewater into the creek. These high flow rates result in large shear flows on the sediment. Both heavy-metal levels (up to 900, 2900 and 6200 mg kg^{-1} of Pb, Cr and Zn, respectively) and polycyclic aromatic hydrocarbons (up to 3300 mg kg^{-1}) were identified as contaminants of concern in the creek sediments. A complicating issue in the creek is the copious gas ebullition from organic matter biodegradation in sediments. These gases can open advective channels that may result in substantial pollution release and compromise cap effectiveness. After modelling the performance of several different kinds of active capping materials for a large range of sediment contaminants, a conceptual design for the active capping demonstration project was proposed. The capping is proposed to be carried out in conjunction with overlying wetlands in the shallow regions of the creek, to remove nutrients from the river and pollutants discharged from combined sewer outflows. Metal and organic contaminant sequestration, and oxidizing agents coupled with a gas collection system, will be evaluated and compared to a sand reference cap.

Key words: active capping, Bubbly Creek, contaminated sediment, Cr, gas ebullition, PAH, Pb, PCB, Zn

INTRODUCTION

Prior to the enactment of the Resource Conservation and Recovery Act in 1976 and the Comprehensive Environmental Response, Compensation and Liability Act in 1980, indiscriminate releases of contaminants to the air, water and soil were largely unregulated and led to substantial pollution of the environment. Contaminants like polycyclic aromatic hydrocarbons (PAHs)

and polychlorinated biphenyls (PCBs) accumulated on the bottom of rivers and lakes, due to their hydrophobicity and relatively long environmental persistence. According to the United States Environmental Protection Agency (USEPA 1998), approximately ten per cent of the sediments underlying US surface waters are contaminated with toxic pollutants. This represents some 1.2 billion yd^3 (0.9 billion m^3) of contaminated sediment, based upon estimates of the total surface sediments in the upper (10 cm) bioactive zone. Even though pollutants in the deeper sediments are generally not directly bioavailable, bioturbation, dredging, navigation, storms and other natural or anthropogenic events frequently disturb the sediments and thus increase contaminant availability to the bioactive zone and water column. Moreover, benthic animals can consume these

Received June 2007; accepted September 2007

Authors

Priscilla Viana, Ke Yin, Xiuhong Zhao and Karl Rockne¹
Department of Civil and Materials Engineering, University of Illinois-Chicago, 3077 Engineering Research Facility, M/C 246, 842 West Taylor St., Chicago, Illinois 60607-7023, USA

1. Corresponding author: krockne@uic.edu

persistent pollutants through bioturbative activities, and may release them to the water phase, contributing to accumulation in the food chain. Increased incidences of fish disease and decreased species biodiversity in pollution-impacted benthic/aquatic environments have been proposed as possible signals of the costs to ecological and human health posed by these contaminants (Malins *et al.* 1987; USEPA 1998).

Contaminated sediment remedial alternatives include dredging and *in situ* capping with sand or clean sediment (Mohan *et al.* 2000; Simpson *et al.* 2002; Bergen *et al.* 2005). Each of these technologies has advantages and disadvantages. Dredging may re-suspend and release contaminants to the water column if effective containment is not maintained. In addition, dredging may be cost-prohibitive in large contaminated areas. Capping is susceptible to contaminant migration, scouring in high-energy environments, and may not be applicable to shallow navigable areas.

A relatively recent innovation in the field of contaminated sediment remediation is active capping. Active capping isolates contaminated sediments from the water phase, while offering degradative and/or contaminant sequestration by the active materials (Viana *et al.* 2006; Zhao *et al.* 2007). Proposed active amendments have included: bioaugmentation (addition of microorganisms); biostimulation through the addition of amendments like oxygen or nitrate to stimulate organisms (Rockne and Strand 1998; Rockne *et al.* 2000; Rockne and Strand 2001); the use of sequestration additives (granular activated carbon, organo-clay, coke, apatite); and the addition of hydraulic sequestration agents such as water-expanding clay (Johnson *et al.* 2002; Murphy *et al.* 2006; Reible *et al.* 2006; Yin *et al.* 2007).

Like normal capping, active capping is also subject to contaminant migration through the cap. However, our previous work has quantitatively demonstrated that selection of appropriate active materials and cap thicknesses can minimize contaminant flux to the water column to levels that are not significant from a risk standpoint – even with significant advective sediment-to-water-column pore-water fluxes. A detailed evaluation of *in situ* processes that might compromise cap effectiveness is vital to guarantee cap effectiveness. We have identified gas ebullition due to methanogenic activity as one of the critical processes in these sedi-

ments, because bubbles are hydrophobic and tend to accumulate hydrophobic contaminants and colloids on their surface. This may possibly result in larger contaminant fluxes to the overlying water column than would occur due to even high-velocity aqueous advective flow. Gas bubble migration may not only release contaminants to the water column and atmosphere (Reible 2005), but may also cause cap damage and even burst the cap (Reible *et al.* 2006), providing additional pathways for contaminant release. Further, scouring of the cap may occur due to high flow velocities in the overlying water column during discharge events.

The site of the present study is known as ‘Bubbly Creek’. Bubbly Creek is the south fork of the south branch of the Chicago River, connecting with the main south branch of the Chicago River at the turning basin. In the early 1900s, Bubbly Creek became a notorious open sewer, as industrial effluents went directly into the stream, as well as wastes from the adjacent stock yards (Sinclair 1906). Although direct wastewater discharge is prohibited now, the creek still is impacted by combined sewer outflow (CSO) effluent on an approximately monthly basis from the Racine Avenue pumping station (RAPS), the largest sewage pumping station in the world. Although these flows can be quite large, up to $6000 \text{ ft}^3 \text{ s}^{-1}$ ($175 \text{ m}^3 \text{ s}^{-1}$) in the 150-ft (46-m)-wide creek, the water in Bubbly Creek is normally stagnant and susceptible to gas ebullition events. The City of Chicago is interested in remediating this historical waterway to provide additional green space to the Canal Origins Park and newly developed residential housing in the area as it changes from industrial to mixed-residential. Towards this goal, a field-scale active-capping demonstration project is being implemented for the turning basin by our research group in collaboration with the Metropolitan Water Reclamation District of Greater Chicago (MWRD); the Wetlands Initiative (TWI); the US Army Corps of Engineers (USACE); and the City of Chicago Department of the Environment (DOE).

MATERIALS AND METHODS

Sampling of Bubbly Creek was performed on board the MWRD RV *PCI* in October and November 2005. A total of 15 sediment cores and 13 surface grabs were

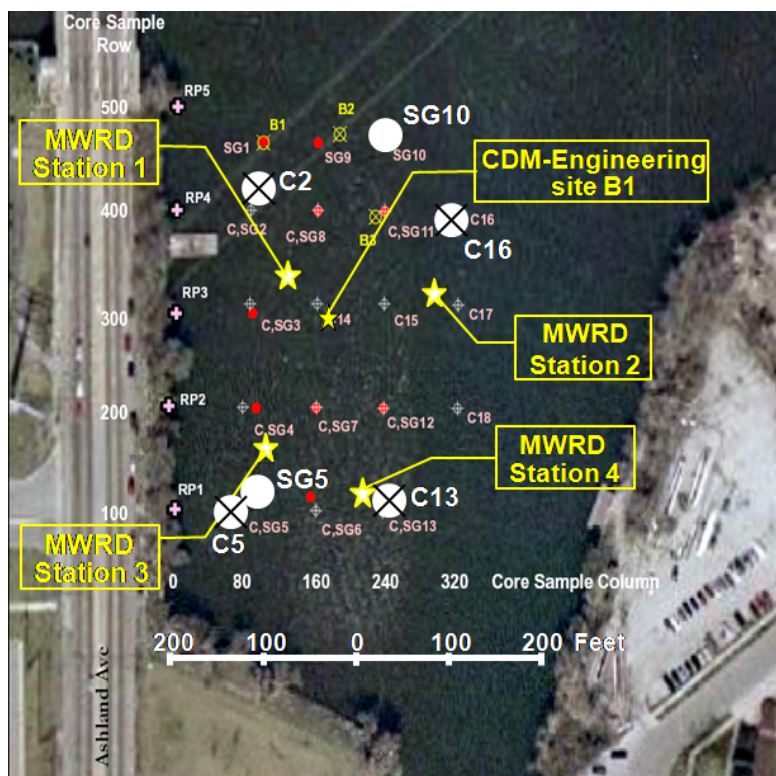


Figure 1. Aerial view at the Bubbly Creek turning basin. Highlighted are selected core (C) and surface grab (SG) locations from the current study. Also shown are MWRD sampling stations and the site of a core sample taken by the USACE in 2004 (CDM-Engineering Site B1). Figure courtesy of Wetlands Initiative.

collected (Figure 1). Four of the cores were full depth to the clay/hardpan layer at a mean depth of 26.2 ft (8 m) below water surface, and the remainder were partial cores to a depth of 6.5 ft (2 m) below the sediment–water interface. A field technician pushed a 2 m × 5 cm diameter plastic core tube into the sediment *in situ* to retrieve intact cores. The cores were sectioned in the field into 20 cm intervals and placed in clean 8 oz (250 mL) glass sample jars with Teflon[®] caps (Fisher Scientific, Pittsburgh, PA). The grab samples were obtained using a nine inch (23 cm) stainless steel dredge and placed in gasketed plastic buckets (5 L, Fisher Scientific, Pittsburgh, PA) and stored in the refrigerator (4°C) until analysis.

Sediment samples were volumetrically sampled from thoroughly homogenized interval segments, using a 3 cm³ syringe as described by Buckley *et al.* (2004). Sediment samples were weighed on a tared, clean disposable aluminium tray and dried (105°C, 48

h). Wet bulk density, per cent moisture, dry bulk density, per cent solids, organic carbon (OC) and organic matter (OM) were analysed (Buckley *et al.* 2004). Anion concentrations in filtered (0.45 µm) pore water were measured by ion chromatography (Dionex IC25, Sunnyvale, CA), as described previously by Rockne and Brezonik (2006).

The 16 EPA priority-pollutant PAHs were extracted from the sediments using a modified Soxhlet extraction method. Wet sediment was ground with anhydrous Na₂SO₄ to complete dryness. The dehydrated sample was transferred to a Whatman cellulose thimble (33 mm × 94 mm, Fisher Scientific, Pittsburgh, PA) and spiked with known amounts of PAH surrogate phenanthrene-D10 (Supelco, Bellefonte, PA). The sediment was then extracted as described in Song *et al.* (2004), in a Soxhlet extractor (Fisher Scientific, Pittsburgh, PA) for 24 h in 150 mL 1:1 (v/v) hexane:acetone mixture. The extract was then cleaned up by elution through a

glass column (30 cm, 1.9 cm i.d. with 250 mL reservoir, Fisher Scientific, Pittsburgh, PA) filled with 20 g of fully activated silica gel (100–200 mesh, Fisher Scientific, Pittsburgh, PA) and dichloromethane, in order to obtain a 1:1 (v/v) hexane:dichloromethane mixture in the column. Extracts were concentrated on a Kuderna–Danish (K–D) concentrator (Fisher Scientific, Pittsburgh, PA) to approximately 5 mL. The volume of sample was then brought up to 10 mL by adding clean solvent. PAH internal standards anthracene-D10, triphenylmethane, benz(a)anthracene-D12 and perylene-D12 (Supelco, Bellefonte, PA) were added to the sample before analysis by gas chromatography mass spectrometry (GC/MS) in EI mode on an Agilent 6890 GC coupled to an Agilent 5973 mass-selective detector. Separation was achieved using an HP-5 MS fused silica capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) and a 5 μL injection volume. The injector temperature was 250°C. The initial column temperature was 50°C; followed by a temperature increase of 10°C min⁻¹ to a temperature of 180°C; a temperature increase of 6°C min⁻¹ to a temperature of 250°C; and a temperature increase of 3°C min⁻¹ to a temperature of 300°C and kept for 5 min. Helium was used as the carrier gas.

Data for PCBs were obtained from a complete composited sediment core taken in the centre of the turning basin by the USACE (2004). PCBs were analysed for total and specific aroclors using USEPA SW-846 method 8082 (USACE 2004). Heavy-metal levels were determined by a contract laboratory for the MWRD, according to USEPA SW-846 method 6010B (USEPA 1996).

Gas production assays were performed with surface-sediment grab samples homogenized (100 mL) and placed into stoppered serum bottles (125 mL, Fisher Scientific, Pittsburgh, PA). The bottles were sparged with N₂ gas and sealed for quiescent incubation at 5°, 20°, 25° or 35°C, upside-down to prevent gas release. Gas production was measured at time points by volume displacement using a 10 cm³ syringe, and the gas phase composition was determined by isothermal gas chromatography with thermal conductivity detection (SRI instruments 9300B, Torrance, CA). The column temperature was maintained at 80°C for five minutes with helium carrier gas.

To better understand the relative efficacy of selected cap materials for containing and/or degrading organic and metal pollutant mixtures, simulations were performed as described in Yin *et al.* (2007). Five capping materials and 22 contaminants were used in the simulations. Performance (as defined by breakthrough curves) was assayed under diffusion only, as follows (Alvarez and Illman 2006):

$$c(x,t) = c_o \operatorname{erfc} \left(\frac{x}{\sqrt{4D_{\text{obs}}t}} \right) \quad (1)$$

$$D_{\text{obs}} = \frac{D_{\text{mol}}\tau}{R} \quad (2)$$

where $c(x,t)$ is the breakthrough porewater concentration of contaminant (mg L⁻¹) at the top of the cap of thickness x at time t (yr); c_o is the initial concentration of contaminant in the sediment porewater (mg L⁻¹); R is the retardation factor (dimensionless); D_{obs} is observed diffusivity (m² yr⁻¹); D_{mol} is the molecular diffusivity (m² yr⁻¹) and τ is the tortuosity of the cap media (dimensionless). All parameters were assumed according to Yin *et al.* (2007).

The mean and maximum depth of scour was calculated to estimate the scouring potential of a sand cap in the creek. The equations for maximum and mean scour depth as a function of cap particle size are as follows (Blodgett and McConaughy 1986):

$$D_{s,\text{max}} = 6.5D_{50}^{-0.115} \quad (3)$$

$$D_{s,\text{mean}} = 1.42D_{50}^{-0.115} \quad (4)$$

where D_{50} refers to the median diameter of the sand cap material, estimated to be 0.6 mm for a sand cap.

Although these equations were developed primarily for non-cohesive (i.e. sand and gravel) soils and the sediments in Bubbly Creek are dominated by cohesive silts and clays (>60%), these results can help us understand the possibility of cap scouring at the creek. The water flow velocity in the 21 channels used to obtain

equations 3 and 4 varied from 4.0 to 7.4 ft s⁻¹ (1.2 to 2.3 m s⁻¹) (Blodgett and McConaughy 1986) and turning basin velocities during peak discharge are within this range.

The critical velocity for initiation of particle suspension in the turning basin was obtained from the data in Van Rijn (1993). The mean water depth in Bubbly Creek was used for calculation of the critical velocity with a D_{50} of 6 mm as before. There is a strong likelihood of severe erosion if water column velocities frequently exceed the critical velocity for initiation of suspension.

RESULTS

The water depth in the Bubbly Creek turning basin (BC TB) ranged from 3 to 14 ft (0.9–4 m); increasing from the east and south shore to the creek centre, with a mean depth of 8.6 ft (2.6 m). The mean depth from water surface to clay hardpan was 26.2 ft (8 m). The estimated total sediment volume is 111 000 yd³ (85 000 m³) in the turning basin. The temperature of the sediment surface core samples varied from 10 to 16.5°C and the water temperature during sample collection was 16°C. Bulk analysis of a homogenized entire sediment core by the USACE (2004) reported that gravel accounts for 2.3% of the solids by mass, with sand, silt and clay accounting for the remaining 32.5, 35.5 and 29.7% of mass, respectively.

An extensive characterization of the solid and moisture content, organic matter and organic carbon content and anion concentration (mainly nitrate and sulfate) was performed. The physical parameters, organic content and PAH results described here are for core samples collected at the four corners of the turning basin (cores 2, 5, 13 and 16). Cores 2, 13 and 16 (Figure 1) are mainly composed of silty mud at the top, transitioning to silty-clay at the bottom. Core 5 is mainly sandy mud at the top transitioning to silty-clay at the bottom. A pronounced naphthalene smell was observed in cores 5, 13 and 16.

Moisture, per cent solids and porosity in the sediment cores are shown in Figure 2. The moisture content of the samples in general decreased with depth, and varied from 42.9% to 66.7% (the mean moisture content was 55.4 ± 5.2%). Porosity reflected the same behaviour, with a mean value of 76.5 ± 4.0%. The wet and dry bulk density and particle density were 1.3 ± 0.1, 0.6 ± 0.1 and 2.4 ± 0.04 g mL⁻¹, respectively.

Sediment OM and OC for cores 2, 5, 13 and 16 are shown in Figure 3. OM varied from 10.4 to 22.0%, with a mean ± standard deviation of 15.3 ± 2.6%, while OC varied from 11.0 to 19.1% (mean ± standard deviation of 14.7 ± 1.7%). These results are typical for carbon-rich, highly reduced nearshore sediments.

PAH data are shown in Figure 4. Seven of the 16 measured PAHs are classified as probable human carcinogens (USEPA 1993): benz[*a*]anthracene (BaA),

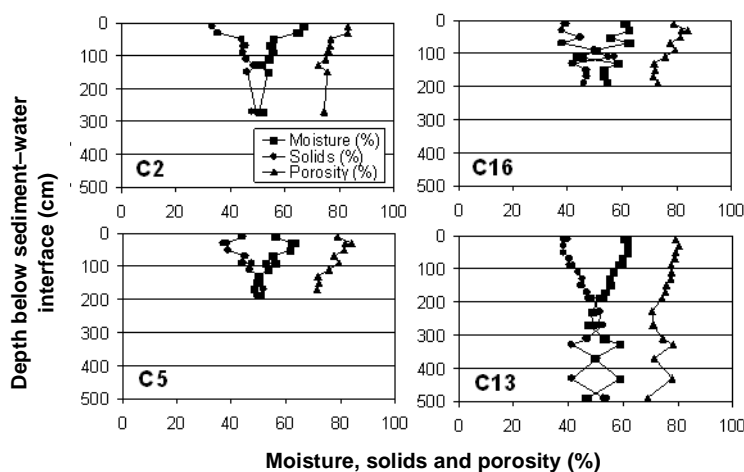


Figure 2. Per cent solids, moisture and porosity versus depth below sediment–water interface for cores 2, 5, 13 and 16 sampled in the Bubbly Creek turning basin. Core locations are shown in Figure 1.

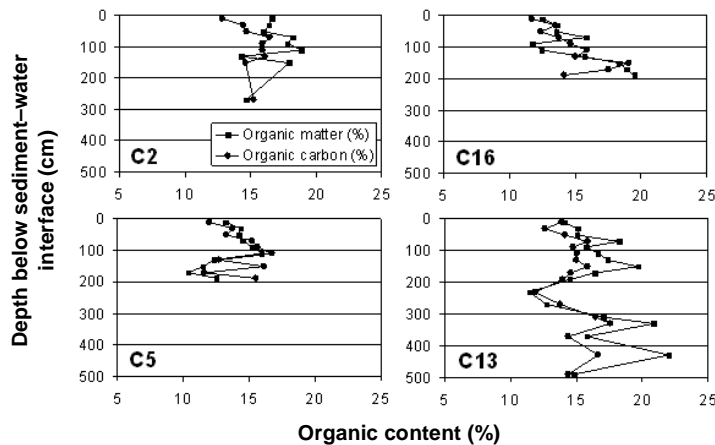


Figure 3. Organic matter and organic carbon versus depth below sediment–water interface for cores 2, 5, 13 and 16 in the Bubbly Creek turning basin. Core locations are shown in Figure 1.

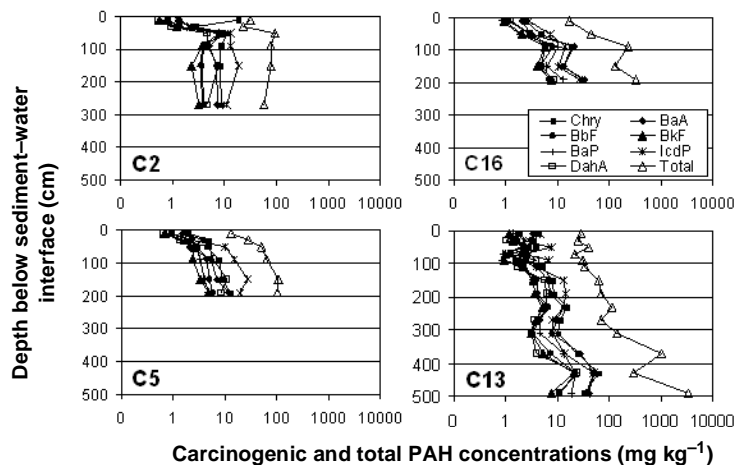


Figure 4. Carcinogenic and total PAH concentrations versus depth below sediment–water interface for cores 2, 5, 13 and 16 in the Bubbly Creek turning basin. Note the logarithmic scale. Core locations are shown in Figure 1.

benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), chrysene (Chry), dibenz[*a,h*]anthracene (DahA) and indeno[1,2,3-*cd*]pyrene (IcdP). Due to their much higher human health impacts (and concomitantly higher risk), we have focused on these compounds here.

Although surficial total PAH concentrations are typically below 100 mg kg⁻¹, deeper sediments have much higher PAH concentrations, even exceeding 1000 mg kg⁻¹ near the clay/hardpan layer (Figure 4). The concentration profile clearly shows that older sediments deposited at the beginning of the last century were

highly polluted with PAHs (the clay/hardpan layer represents the original construction of the turning basin in the late 1800s). The creek has received large amounts of organic and inorganic pollution from industrial waste runoff, as well as stormwater and CSO discharges (USACE 2004).

Mean sediment PAH levels for all core samples were compared to National Oceanic and Atmosphere Administration (NOAA) guidelines for contaminated sediments (NOAA 1999). NOAA guideline values are, for preliminary screening purposes in freshwater sediment for the upper effects threshold (UET), defined as

the lowest concentration above which adverse biological impacts would always be expected due to exposure to that concentration alone. With the lone exception of benzo[*k*]fluoranthene, all other PAHs were present in turning basin sediments at much higher concentrations than the NOAA UET guidelines (Figure 5).

The total PAH mass in the turning basin sediment is estimated to be 6600 kg. These elevated PAH levels suggest the need for active cap amendments with high organic sorption capacity. Granular activated carbon (GAC), organo-clay and coke have all been proposed as potentially good sequestration agents capable of reducing release and breakthrough of PAHs through the cap.

Total and specific aroclor concentrations are shown in Figure 6. Although the Illinois Environmental Protection Agency (IEPA) does not have criteria for specific aroclors, the total PCB levels in the turning basin exceed the 'extreme elevated' (EE) criterion used by IEPA (Kelly and Hite 1984) (Figure 6).

Heavy-metal levels in Bubbly Creek sediments are shown in Figure 7. Comparing pollutant levels with both toxic threshold limit concentrations (TTL) provided by the State of California Assessment Manual (CAM) (CDHS 1981) and EE values used by IEPA (Kelly and Hite 1984), demonstrate that heavy-metal

concentrations in the turning basin sediment may present a threat to ecological and/or human health. Although no metal exceeds CAM criteria, Cr, Cu, Pb, Zn and Hg are all well above IEPA EE criteria. These elevated metal concentrations suggest the need for active capping amendments able to bind metals into insoluble and/or non-bioavailable phases. Apatite would be an option, as it sequesters metals by continuously supplying phosphate to solution to exceed the solubility limits of various metal-phosphate phases (e.g. pyromorphite and autunite for Pb).

The presence of both heavy-metal and hydrophobic organic contaminants at levels of concern necessitate selection of capping materials effective at the combined treatment of mixtures. Therefore, GAC, coke, shredded tires and organo-clay were investigated as possible cap materials. Although apatite is reported to be an effective amendment for metal sequestration, our preliminary simulations suggest that it is less effective for organic contaminant sequestration than GAC is for metal sequestration. The time for breakthrough of over 20 different contaminants in different cap materials under different environmental conditions was modelled as in Yin *et al.* (2007).

Figure 8 is an example of diffusive transport of phenanthrene, pyrene and Pb (at pH 4 and 9) in differ-

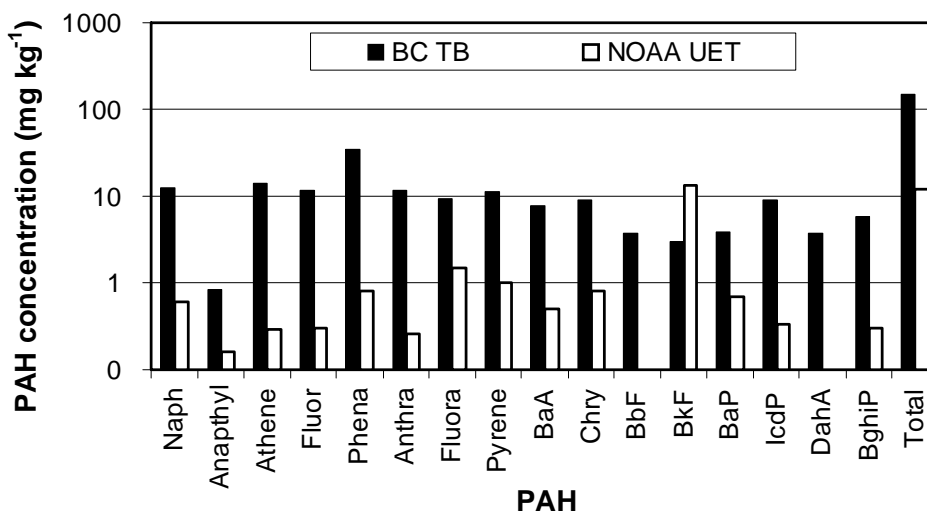


Figure 5. Mean PAH concentrations in all Bubbly Creek turning basin (BC TB) core samples, compared with NOAA guidelines for upper effects threshold levels (UET) for freshwater sediments. Note the logarithmic scale on the y axis.

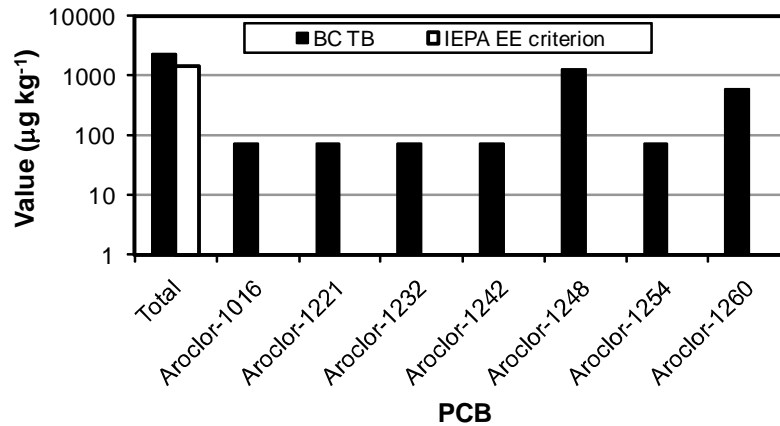


Figure 6. Total and specific aroclor concentrations of a complete composited sediment core from USACE (2004) compared to the IEPA criterion to classify stream sediments. Note the logarithmic scale on the y axis. Core location is shown in Figure 1.

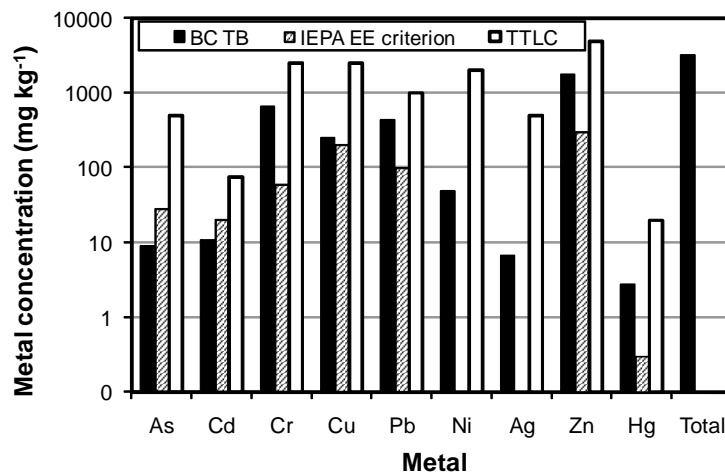


Figure 7. Total and specific metal content of a complete composited sediment core in Bubbly Creek turning basin sediments (USACE 2004) compared to IEPA stream sediment classification (Kelly and Hite 1984) and CAM criteria. Note logarithmic scale on the y axis. Core location is shown in Figure 1.

ent cap materials. The effects of porewater pH on the breakthrough of the pH-sensitive metals Pb, Cr and Cd were studied. It was observed that the time needed for breakthrough will be longer for higher molecular weight PAHs like pyrene, than for lower molecular weight PAHs like phenanthrene. Similar behaviour was observed for more highly chlorinated PCBs. The results clearly demonstrate that cap thickness is the most important parameter determining breakthrough

time for metals – even more than choice of cap material (Figure 8).

As noted in the introduction, cap integrity is dependent upon cap scouring by hydraulic forces and gas ebullition due to methanogenic degradation of organic matter. Because Bubbly Creek has high surface-water velocities during RAPS discharge events, we analysed erosion effects considering a predicted maximal velocity of 6.5 ft s^{-1} (2 m s^{-1}). With this

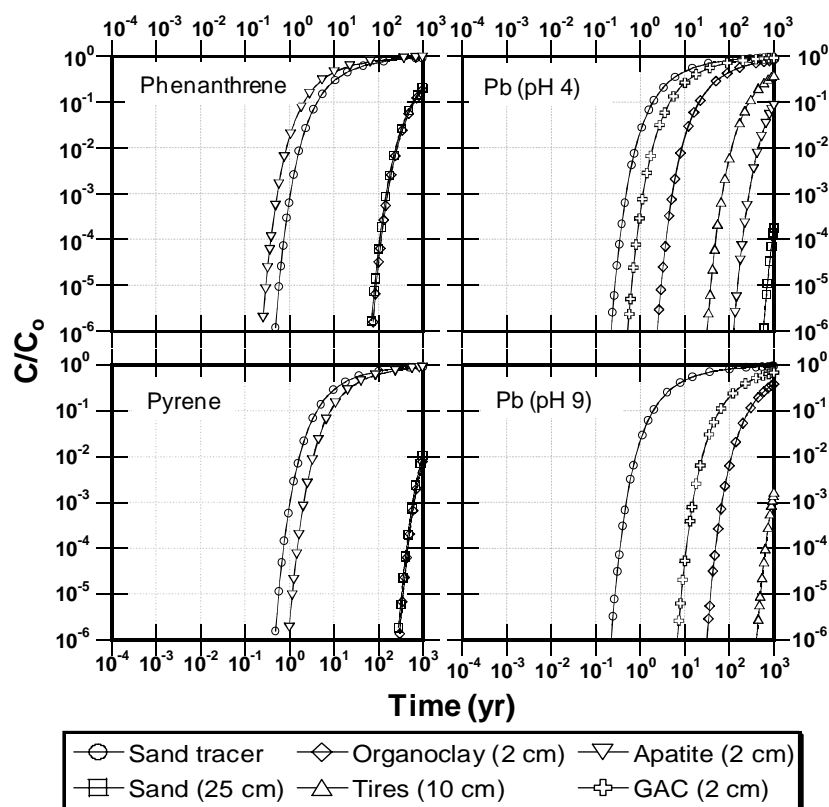


Figure 8. Breakthrough concentration of phenanthrene, pyrene and Pb (at pH 4 and 9) in different cap materials (25 cm sand, 2 cm organo-clay, 10 cm shredded tire, 2 cm apatite and 2 cm GAC) under static conditions. Also shown is the transport of a conservative tracer in the sand cap, for comparison. Note the logarithmic scale on both axes.

value, the mean scour depth for a sand cap would be 1 m, and depths exceeding 2 m could be reached without sufficient armouring. Moreover, the critical velocity for initiation of suspension was 2.2 ft s^{-1} (0.7 m s^{-1}), which is well below the maximal velocities expected during a discharge event. These results indicate that armouring of the site must be considered – particularly in the main channel where the highest velocities were predicted to occur. More detailed data collection and modelling efforts are being undertaken to determine more precisely the erosion potential in the creek proper.

Experiments to measure gas production rates in two sites along the creek were performed as a function of temperature, and were modelled using the Arrhenius equation. The results show that gas production varied substantially as a function of temperature, but not with site location. The biogenic gas production reaction rate

constant k was calculated for each site, assuming a zero order rate law (other rate laws were considered but did not fit the kinetic data). Rate constants were plotted on an inverse temperature Arrhenius plot to obtain the activation energy for methanogenesis (E_a) as in Viana *et al.* (2007). The mean E_a of methanogenesis was $42.5 \pm 8.1 \text{ kJ mol}^{-1}$. Our results are similar to methanogenic E_a values reported in the literature (Thebrath *et al.* 1993; Prieme 1994; Chou *et al.* 2004), which range from 27 to 138 kJ mol^{-1} . The lowest observed E_a values were with simple defined substrates (phenol), and the higher values were reported with more complex organic compounds like fulvic acids and humic acids commonly found in peat soil.

Using these kinetic data, we were able to predict the amount of gas that could be produced during an entire year for the upper 1 m of sediment (the most active zone with the greatest ebullition potential) and decide

whether gas control systems would be necessary. Even though neither site produced gas in excess of its own volume on an annual basis, the amount of gas produced was still considerable (Figure 9). It is entirely possible that the sediment will be disturbed during cap placement and it may stimulate higher rates of gas production. Therefore, gas control will likely be adopted for this site, to ensure cap integrity.

A further important consideration is the composition of the biogenic gas. The ratio of methane to carbon dioxide in biogenic gas produced from the BC TB sediments is also shown in Figure 9. The CH_4/CO_2 ratio was clearly affected by temperature. These results suggest strongly that changes in microbial community composition took place as a function of incubation temperature. Hydrogenotrophic methanogens produce only methane (while consuming CO_2 and H_2), while acetoclastic methanogens produce CH_4 and CO_2 . The finding that lower CH_4/CO_2 ratios were observed in sediment incubated at lower temperatures suggests the dominance of acetoclastic methanogens at lower temperatures, while hydrogenotrophic methanogens become dominant at higher temperatures, thus increasing the CH_4/CO_2 ratio.

The conceptual design for the Bubbly Creek active capping demonstration project is shown in Figure 10. The focus of the design is on the sequestration of both metal and organic pollutants. The impact of high flows on cap scouring will be determined by having both a sub-aqueous area exposed to high shear flows and an

enclosed wetland-covered area. Four capping strategies will be used in both the enclosed and open areas: sand, GAC/geotextile, apatite/clay and nitrate-salt amended. Each treatment will address different mechanisms for active capping: sand as the reference site; GAC for organic sequestration (our simulations suggest that it will not work well in sequestering heavy metals); apatite/clay for metals; and a hydraulic barrier and nitrate to stimulate the anaerobic biodegradation of organics and oxidation of sulfides. Dry active capping materials will be sandwiched between geotextile fabric layers laid on the contaminated sediments. An overlying permeable sand layer will then be placed on top of the active capping material and covered with a highly permeable GeoNet layer to facilitate lateral gas transport. This will allow evolved biogenic gas to be captured and channelled to the side shoreline. On top of the GeoNet will be wetland fill in the shallow zones near the shore (Figure 10). The purpose of the wetland is to provide habitat and nutrient removal for the Chicago River water diverted through the wetland. During construction, monitoring tubes will be placed on top of the sediment, on top of the active capping layer and on top of the permeable sand layer to provide long-term continuous monitoring of contaminant release. A walkway will be developed on the separation between the wetland and sub-aqueous cap areas, to allow public use and monitoring of the facility following construction.

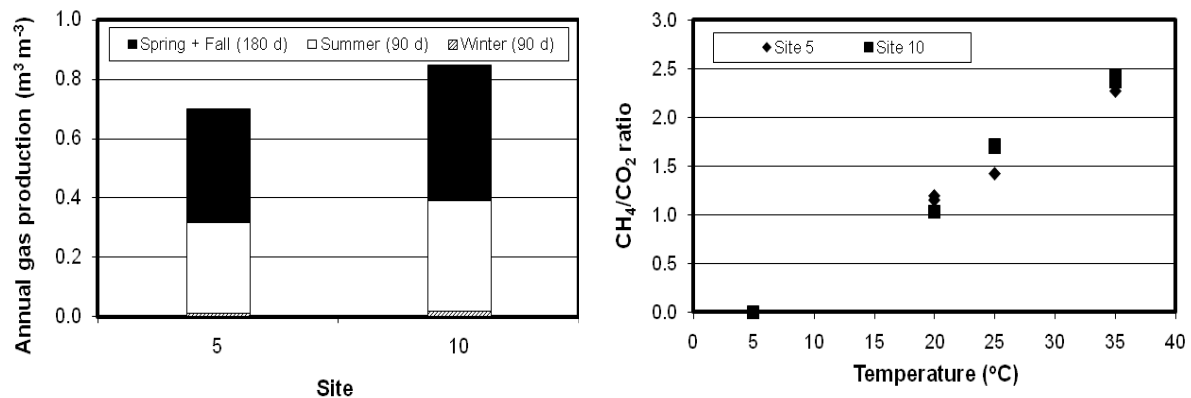


Figure 9. Estimated annual volumetric gas production ($\text{m}^3 \text{m}^{-3}$ of sediment) and CH_4/CO_2 ratio of biogenic gas produced in Bubbly Creek turning basin surficial sediments. Site locations are shown in Figure 1.

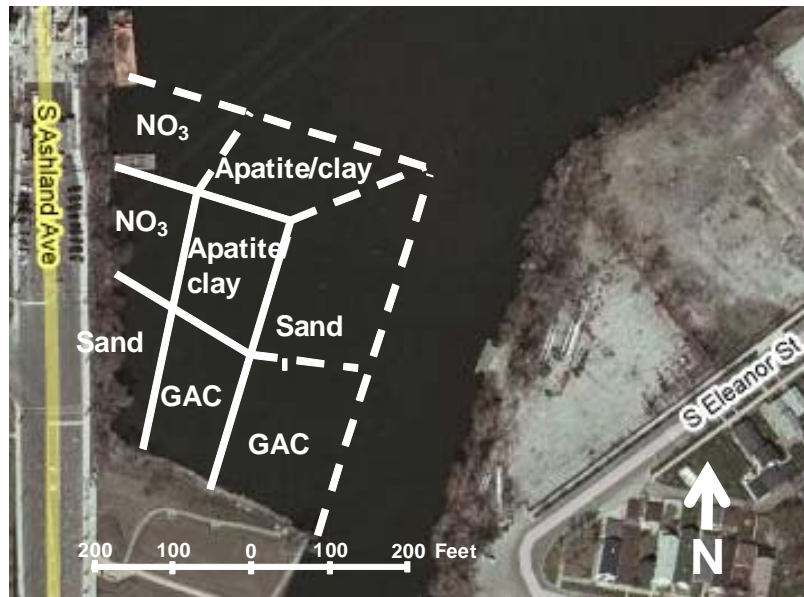


Figure 10. Capping demonstration project at the Bubbly Creek turning basin. Subaqueous cap is represented by dashed lines, and wetland-covered cap by solid lines in the shallow nearshore zone. Base satellite photo from Google – Map data ©2007 NAVTEQ™.

CONCLUSIONS

Characterization of the sediments at the Bubbly Creek turning basin showed the presence of mixed heavy-metal and organic contamination. Concentrations of Pb, PCBs and PAHs were as high as 900 mg kg^{-1} , 2.3 mg kg^{-1} and 3270 mg kg^{-1} , respectively. These concentrations exceed both IEPA criteria for stream sediments and NOAA guidelines for preliminary screening purposes in freshwater sediment. Four different active capping strategies will be employed (sand, GAC/geotextile, apatite/clay and nitrate-salt amended) in both a sub-aqueous area exposed to higher shear flows during RAPS discharge events and an enclosed wetland-covered area. Long-term flux monitors will be employed in conjunction with cap construction to allow detailed examination of cap component effectiveness.

ACKNOWLEDGEMENTS

This work was supported by grant BES-0348512 from the National Science Foundation, and a grant from the Wetlands Initiative for sediment restoration. We wish

to express our gratitude to MWRD for data and the use of RV *PCI* for sample collection; to the USACE for use of data; to Patrick Engineering for coring; and to the Wetlands Initiative for use of the base sample location map.

REFERENCES

- Alvarez, P.J. and Illman, W.A. (2006) *Bioremediation and Natural Attenuation: Process Fundamentals and Mathematical Models*. Wiley, Hoboken, NJ
- Bergen, B.J., Nelson, W.G., Mackay, J., Dickerson, D. and Jayaraman, S. (2005) Environmental monitoring of remedial dredging at the New Bedford Harbor, MA, Superfund Site. *Environ. Monit. Assess.*, **111** (1–3), 257–275
- Blodgett, J.C. and McConaughy, C.E. (1986) *Rock Riprap Design for Protection of Stream Channels Near Highway Structures, Vol. 2 – Evaluation of Riprap Design Procedures*. Water-Resources Investigations Report 86-4128. US Geological Survey, Sacramento, CA
- Buckley, D.R., Rockne, K.J., Li, A. and Mills, W.J. (2004) Soot deposition in the Great Lakes: implications for semi-volatile hydrophobic organic pollutant deposition. *Environ. Sci. Technol.*, **38** (6), 1732–1739

- CDHS (1981) *California Assessment Manual for Hazardous Wastes*. California Department of Human Services, Sacramento, CA
- Chou, H.-H., Huang, J.-S. and Hong, W.-F. (2004) Temperature dependency of granule characteristics and kinetic behavior in UASB reactors. *J. Chem. Technol. Biotechnol.*, **79**, 797–808
- Johnson, K.M., Smith, M.L. and Lowry, G.V. (2002) *Sediment Management in the Anacostia and Grasse River: Applying Fe(0)-based Reactive Sediment Caps for in situ PCB Destruction* (Progress Report 9/1/02). It can be found online at <http://www.hsrb-ssw.org/cap-amend1.pdf>
- Kelly, M.H. and Hite, R.L. (1984) *Evaluation of Illinois Stream Sediment Data, 1974–1980*. Illinois Environmental Protection Agency. Springfield, IL (IEPA/WPC/84-004)
- Malins, D.C., McCain, B.B., Brown, D.W., Varanasi, U., Krahn, M.M., Myers, M.S. and Chan, S.-L. (1987) Sediment-associated contaminants and liver diseases in bottom-dwelling fish. *Hydrobiologia*, **149** (1), 67–74
- Mohan, R.K., Brown, M.P. and Barnes, C.R. (2000) Design criteria and theoretical basis for capping contaminated marine sediments. *Appl. Ocean Res.*, **22** (2), 85–93
- Murphy, P., Marquette, A., Reible, D. and Lowry, G.V. (2006) Predicting the performance of activated carbon-, coke- and soil-amended thin layer sediment caps. *J. Environ. Eng.-ASCE*, **132** (7), 787–794
- NOAA (1999) *Screening Quick Reference Tables*. National Oceanic and Atmosphere Administration (*Hazmat Report 99-1*)
- Prieme, A. (1994) Production and emission of methane in a brackish and a freshwater wetland. *Soil Biol. and Biochem.*, **26** (1), 7–18
- Reible, D. (2005) In situ sediment remediation through capping: status and research needs. Paper presented at the SERDP workshop on research needs in contaminated sediments, Charlottesville, VA, October 2004. The paper may be downloaded from <http://www.hsrb-ssw.org/pdf/cap-bkgd.pdf>
- Reible, D., Lampert, D., Constant, D., Mutch Jr., R.D. and Zhu, Y. (2006) Active capping demonstration in the Anacostia River, Washington, D.C. *Remediation J.*, **17** (1), 39–53
- Rockne, K.J. and Brezonik, P.L. (2006) Nutrient removal in a cold-region wastewater stabilization pond: Importance of ammonia volatilization. *J. Environ. Eng.-ASCE*, **132** (4), 451–459
- Rockne, K.J. and Strand, S.E. (1998) Biodegradation of bicyclic and polycyclic aromatic hydrocarbons in marine anaerobic enrichments. *Environ. Sci. Technol.*, **32** (24), 3962–3967
- Rockne, K.J. and Strand, S.E. (2001) Anaerobic biodegradation of phenanthrene, naphthalene and biphenyl by a denitrifying enrichment culture. *Water Res.*, **35** (1), 291–299
- Rockne, K.J., Chee-Sanford, J.C., Hedlund, B.P., Sanford, R.A., Strand, S.E., Leigh, J., Staley, J.T. (2000) Anaerobic polycyclic aromatic hydrocarbon degradation by marine microbial isolates under nitrate-reducing conditions. *Appl. Environ. Microbiol.*, **66** (4), 1595–1601
- Simpson, S.L., Pryor, I.D., Mewburn, B.R., Batley, G.E. and Jolley, D. (2002) Considerations for capping metal-contaminated sediments in dynamic estuarine environments. *Environ. Sci. Technol.*, **36**, 3772–3778
- Sinclair, U.B. (1906) *The Jungle*. Doubleday, New York
- Song, W.L., Ford, J., Li, A., Mills, W.J., Buckley, D.R. and Rockne, K.J. (2004) Polybrominated diphenyl ethers in the sediment of the Great Lakes. 1 – Lake Superior. *Environ. Sci. Technol.*, **38** (12), 3286–3293
- Thebrath, B., Rothfuss, F., Whiticar, M.J. and Conrad, R. (1993) Methane production in littoral sediment of Lake Constance. *FEMS Microbiol. Ecol.*, **102**, 279–289
- USACE (2004) *Collection and Analysis of Sediment Samples from the South Fork South Branch, Chicago River*. Draft final report prepared by CDM Consultants
- USEPA (1993) *Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons*. US Environmental Protection Agency (EPA/600/R-93/089)
- USEPA (1996) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (Method 6010b)*. US Environmental Protection Agency (EPA/SW-846)
- USEPA (1998) *EPA's Contaminated Sediment Management Strategy*. US Environmental Protection Agency, Washington, D.C. (EPA-823-R-98-001)
- Van Rijn, L.C. (1993) *Principles of Sediment Transport in Rivers, Estuaries and Coastal Seas*. Aqua Publications, Amsterdam
- Viana, P.Z., Yin, K., Zhao, X. and Rockne, K.J. (2006) Active capping: a low cost technology to contain and reduce the exposure risk of contaminated sediments. In: *7th Regional Conference of USA Inter-American Association of Sanitary Engineering and Environmental Sciences, Chicago, IL*
- Viana, P.Z., Yin, K., Zhao, X. and Rockne, K.J. (2007) Modeling and control of gas ebullition in capped sediments. Paper D-027. In: Foote, E.A. and Durell, G.S. (conference

chairs) *Remediation of Contaminated Sediments 2007. Proceedings of the Fourth International Conference on Remediation of Contaminated Sediments*. ISBN 978-1-57477-159-6. Battelle Press, Columbus, OH

Yin, K., Viana, P.Z., Zhao, X.H. and Rockne, K.J. (2007) A Monte Carlo simulation approach for active caps in mixed contaminant environments. Paper D-018. In: Foote, E.A. and Durell, G.S. (conference chairs) *Remediation of Contaminated Sediments 2007. Proceedings of the Fourth International Conference on Remediation of Contaminated*

Sediments. ISBN 978-1-57477-159-6. Battelle Press, Columbus, OH

Zhao, X., Viana, P.Z., Yin, K. and Rockne, K.J. (2007) Combined active capping/wetland demonstration in the Chicago River. Paper D-019. In: Foote, E.A. and Durell, G.S. (conference chairs) *Remediation of Contaminated Sediments 2007. Proceedings of the Fourth International Conference on Remediation of Contaminated Sediments*. ISBN 978-1-57477-159-6. Battelle Press, Columbus, OH

Apart from fair dealing for the purposes of research or private study, or criticism or review, this publication may not be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photographic or otherwise, without the prior permission in writing of the publisher.

The views expressed in this and in all articles in the journal *Land Contamination & Reclamation* are those of the authors alone and do not necessarily reflect those of the editor, editorial board or publisher, or of the authors' employers or organizations with which they are associated. The information in this article is intended as general guidance only; it is not comprehensive and does not constitute professional advice. Readers are advised to verify any information obtained from this article, and to seek professional advice as appropriate. The publisher does not endorse claims made for processes and products, and does not, to the extent permitted by law, make any warranty, express or implied, in relation to this article, including but not limited to completeness, accuracy, quality and fitness for a particular purpose, or assume any responsibility for damage or loss caused to persons or property as a result of the use of information in this article.