Analysis of Heavy Metals in Canal Sediments to Gain a Better Insight into Current and Future Canal Management Strategies

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Canal and Waterway Management

- Historical industrial route
  - Coal, glass and metal-working
  - Approximately 257 km of waterways during peak operation

- Leisure Route
- Maintenance includes
  - 160 km open to navigation
  - Depth maintenance
  - Towpath clearing
  - Refuse collection

Connected to national canal systems at a number of intersections

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Canal Maintenance

- Depth maintenance
  - 25 year plan in urban canals
  - 40 year plan in rural canals
  - 8 year survey period
  - Dredging as required at confluences, inlets

- Removal carried out in stages
  - Canal sediment modelling/hydrographic surveys
  - Sectional dredging
  - Sediment disposal via incineration/landfill
Background, Aim and Objectives

- Dredging expenses in 2014 totalled £4.4m
- Canal & River Trust intend to invest £8-10M a year for the next decade on canal maintenance
- Canal & River Trust identified current disposal methods as an area for improvement by
  - Recovering and recycling contaminants present in the sediments
  - Reducing the volume of waste sent to landfill
Background, Aim and Objectives

- **Aim** to improve maintenance sustainability by developing a better understanding of canal sediment contamination

- **Objectives of the project** were to:
  - Identify constituent compounds/elements in canal sediments that require remediation or are recoverable based on value of recycling
  - Evaluate processes that may allow efficient recovery of target constituents
  - Investigate economic feasibility of potential scale up options
  - Measuring sediment accretion to enhance dredging plans
Elements of Interest

- 32 elements targeted
  - 6 heavy metals shown
  - Environmental Regulations
  - Economic Potential
- Legislation Directives
  - 2006/11/EC-Dangerous substances in the aquatic environment
  - 1999/31/EC; 2003/33/EC - Landfill

<table>
<thead>
<tr>
<th>Target Element</th>
<th>Landfill Limit /mg kg(^{-1})</th>
<th>Leach limit /mg l(^{-1})</th>
<th>EQS /µg l(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.4</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>Cd</td>
<td>0.6</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>4</td>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td>Pb</td>
<td>5</td>
<td>3</td>
<td>50</td>
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</table>

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<tr>
<th>Target Element</th>
<th>Historical Applications</th>
<th>Current Applications</th>
</tr>
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<tbody>
<tr>
<td>Co</td>
<td>Ceramic and Glass Pigment</td>
<td>Temperature/Corrosion resistant alloys, nanotechnology and chemical industries. 30,680 USD/t. source LME</td>
</tr>
<tr>
<td>Mn</td>
<td>Ceramic and Glass Pigment, Steel Production</td>
<td>Steel and alloy production. Year end value-2,350 USD/t. source ICE</td>
</tr>
</tbody>
</table>
Metals Recovery Method

• Total Digest significant higher recovery

• Aqua Regia (AR) digest used on canal sediment samples

CERTIFIED REFERENCE MATERIALS (CRM)
• SO3/SO4 sediments certified from 40 separate labs
• STSD-2 provisional values

Error bars represent 2 std deviations
Metal Concentration and distribution

![Graph showing Arsenic and Cadmium concentrations in different locations.](image)

**Target Element**

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<td>EQS /µg l(^{-1})</td>
<td>10</td>
<td>5</td>
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</table>

Error bar represent 95% confidence intervals for each location.
Metal Concentration and distribution

Chromium

C (mg/kg)

Depth in Canal Bed (cm)

Cobalt

C (mg/kg)

Depth in Canal Bed (cm)

Lead

C (mg/kg)

Depth in Canal Bed (cm)

Manganese

C (mg/kg)

Depth in Canal Bed (cm)

Location 1  Location 2  Location 3  Location 4  Location 5

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Management Strategies

Areas for improvement

- Recovering and recycling contaminants present in the sediments
- Reducing the volume of waste sent to landfill

Drivers behind improvement

- Environmental and economic considerations for current practice versus potential management practice
- Concentration of analytes in the sediment may at a level requiring disposal to hazardous landfill (sustainability issues)
- Current practice of blending requires analytical service costs and availability of uncontaminated material (sustainability issues)
- Economics also extend to associated transport and disposal* costs.

*dredging activities are exempt from landfill taxes
Management Strategies

• Improved knowledge on distribution and concentration of heavy metals targeted management/treatment of sediment

• Targeted treatment
  – Less inert material for blending
  – Carry out targeted remediation allowing recovery of materials

• Recovery of materials
  – Metals and inorganic constituents
  – Sediment

• Any recovery method must be economically and environmentally viable

<table>
<thead>
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<th>Heavy Metal</th>
<th>Lowest mean concentration /mg kg$^{-1}$</th>
<th>Landfill limit /mg kg$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>As</td>
<td>34.1 ± 8.1 location 1</td>
<td>0.4</td>
</tr>
<tr>
<td>Cd</td>
<td>20.0 ± 1.4 location 5</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>241.7 ± 15.7 location 1</td>
<td>4</td>
</tr>
<tr>
<td>Pb</td>
<td>790.7 ± 80.9 location 4</td>
<td>5</td>
</tr>
</tbody>
</table>
Summary

- Comprehensive sampling-Depth and Location
- Constituent concentration depth, location and element specific
  - Aqua Rega digest does not provide absolute recovery data
- Depth and location data allows the possibility of targeted remediation
- Recovery of constituents and sediment material
- More work needed in inorganic and organic constituent identification

Sustainable canal management

Environmental impact

Value offset

Inorganic constituents

Organic components

Sediment solids

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Acknowledgements

- **John Hinchcliffe and Brian Vincent** – Design and manufacture of sampling and extraction equipment

- **Adele Lawrence, Priscilla Cavalheiro Mendes Moitta, Xiao-Xi Liu and Hannah Beska** – Sampling and analytical support

- **Dave Clift** – Sample extraction and analytical support

- **Victoria Taylor** – Hydrographic survey and current sediment management practices
Core Extraction (3cm depth x 6.4cm diameter) → Oven Dry (60°C max, 24hrs) and ground sediment

Microwave digest stage 1: 10ml HNO₃, 1hr 190°C → Oven Dry (60°C max, 24hrs) Weigh 0.5g

Microwave digest stage 2: 2ml HCl + 5ml HF, 40mins 190°C → Microwave digest stage 3: 30ml 4% boric acid, 30mins 170°C

Analysis by ICP-AES spectrometry → Make up to 100ml with 18.2 MegΩ water

Core Extraction oven dry (60°C, 24hrs) → Sediment ground to fine powder

Aqua Regia Digest: 20ml; Temperature 20-120°C → Oven Dry. 1g of sample weighed

AR Digest: 20ml; 120°C for 2-8 hrs, AR Digest: 10ml 10%v/v HNO₃; 120°C for 30mins → Increase to 100mL with 10%v/v HNO₃; Centrifuge

Reconstitute to 40mL with 10%v/v HNO₃; Centrifuge → Sample analysis using ICP-AES