

## Conference Proceedings

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# Investigating historical releases of industrial and combustion particles using urban ponds

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### Abstract

Receiving particles from a range of anthropogenic sources, urban ponds are important ‘sinks’ of air pollution. A small pond set within the industrial heartland of North West England, UK has yielded a depositional history of particulate matter pollution (PM) spanning the 20<sup>th</sup> century. This unique sediment record has allowed past emissions of pollution particulates to be retrospectively characterised.

A high-resolution history of air pollution has been reconstructed using a range of environmental analyses including environmental magnetism and x-ray fluorescence, supported by isotope chronologies. The size and elemental composition of individual particulates from 1970 have been characterised using scanning electron microscope analysis with energy dispersive spectroscopy to reveal insights into PM source and toxicity. High temperature combustion processes, metallurgy, roadways and scrap heaps are potential sources of particles observed.

Set amongst the populations most at risk to the long-term health effects of PM, urban ponds are unique sedimentary archives, capturing temporal variations in the deposition of pollution. This work demonstrates how historical releases from industry and combustion processes can be rediscovered, extending our understanding of urban PM back in time beyond contemporary monitoring techniques.

*Keywords: Pond sediments; air pollution; combustion particulates; industry; urban particulate matter.*

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### 1. Introduction

Investigating long-term releases of PM in the urban environment is important due to the known toxicity of ‘inhalable’ particles, in particular PM<sub>10</sub> (<10 µm) (Harrison et al., 2010).

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Assessing the cumulative effects of pollutants over life-time exposures, or time lags between exposure and disease occurrence are restricted given that historical PM data are limited. Air quality monitoring stations have measured PM<sub>10</sub> concentrations in the UK since 1992. Prior to this only sulphur dioxide and black smoke data are available (post-1960). These data however, do not reveal information regarding the composition, size or source of particles and therefore, little is known about the 'nature' of past emissions or how air quality has changed throughout the 20<sup>th</sup> century, a time of industrial advancements, urban developments, increased road and air travel, and progressively stringent air pollution controls.

Urban ponds are unique archives of environmental change and can be used to reconstruct histories of air pollution. Set within the urban landscape, they receive a complexity of PM from surrounding local (short-range) industrial and traffic sources as well as regional (long-range) emissions (Power & Worsley, 2009). Particles settle through the water column and deposit on the pond basin. Under suitable conditions, ponds that have proven longevity can yield a history of PM deposition, as pollution particulates are preserved within their naturally accumulating sediments (Fig. 1). Understanding site-specific releases of PM within a heavily industrialised landscape is imperative for rediscovering what types of air pollution local populations have been exposed to over time to determine possible environment health relationships.

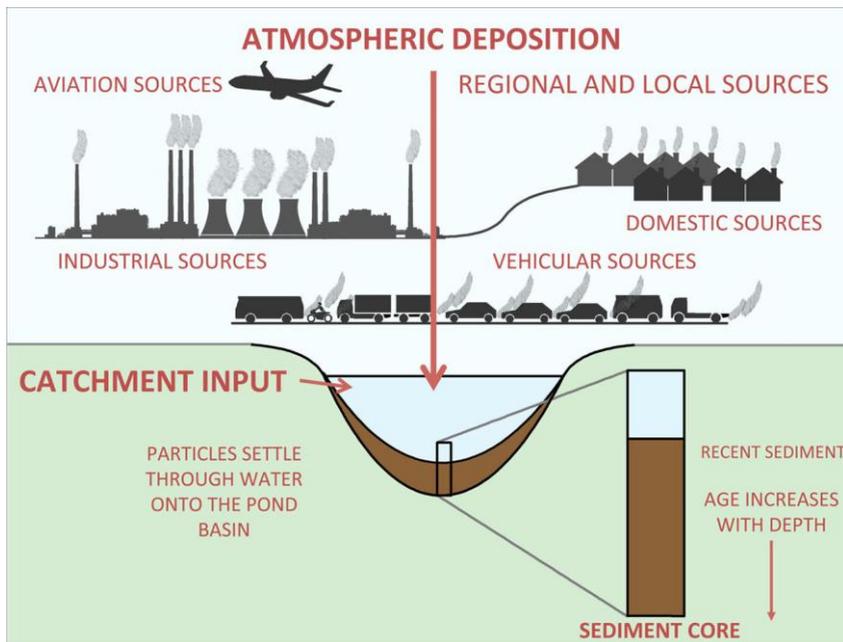


Fig. 1. Urban ponds as archives of air pollution.

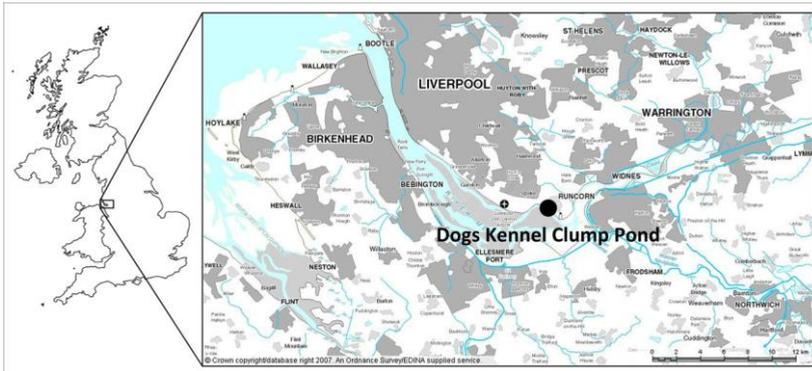


Fig. 2. Location of Dogs Kennel Clump Pond in North West England, UK.

## 2. Site description

Set within a heavily industrialised landscape in North West England in the UK, sediment cores were extracted from the centre of a small (1650 m<sup>2</sup>) manmade pond ‘Dogs Kennel Clump’ (DKC) in Hale, south Merseyside (National Grid Reference: SJ 46344, 82105) (Fig. 2). Renowned as the historical birthplace of the UK Industrial Revolution and heartland for the modern British chemical industry, the Merseyside area has experienced industrial intensification since the early 1800s, with further industrial expansions and diversification throughout the 20<sup>th</sup> century. Nearby industries at Halewood (<2.5 km to the west) include a car manufacturing site, chemical and pharmaceutical factories, foundries and concrete works, which were established during the mid 20<sup>th</sup> century. DKC is also <3.5 km (east) from John Lennon International Airport and <4 km (west) from two heavily industrialised towns: Runcorn and Widnes.

## 3. Method

Sediment cores were extruded into 0.5 cm (upper 10 cm of sediment) and 1 cm (below 10 cm) intervals. Analyses including environmental magnetism, geochemistry and isotope dating were applied to reconstruct an environmental history of the site (Table 1). Sediment from 1970 (4-4.5 cm) was further analysed using SEM-EDS to image and characterise particles.

Table 1. Explanation of methods used.

Method	Explanation
Magnetic susceptibility ( $\chi_{LF}$ )	A small magnetic field was applied to ‘magnetise’ iron oxides within samples. Values indicate the concentration of ferrimagnetic minerals (Walden et al., 1999), including iron oxides produced from the combustion of fossil fuels (Mageria et al., 2013).
Geochemistry	Bulk elemental composition of samples were determined using energy dispersive x-ray fluorescence (XRF) analysis and normalised for organic content (via loss on ignition at 450°C) (Boyle 2001). Lead, Zn and S concentrations are presented as proxies for anthropogenic emissions. Sediment cores were dated based on the radioactive decay of <sup>137</sup> Cs and <sup>210</sup> Pb isotopes. Dates were calculated using a constant rate of supply model (Appleby & Oldfield, 1978).
Isotope chronology	
SEM-EDS	High resolution imaging was achieved using scanning electron microscopy combined with energy dispersive spectroscopy to determine the elemental composition of individual particles.

A ‘closed system’ DKC pond has no drainage inputs or outflows and its small catchment is defined by steep, heavily vegetated pond margins. This high pond-to-

catchment ratio (1:1.23) results in pond sediments whose main inorganic components are derived from the atmosphere. The integrity of the sediment record is supported by intra-site agreement of magnetic concentration profiles and the achievement of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  isotope chronologies. Furthermore, inter-site similarities of trends in spheroidal carbonaceous particles, unambiguous indicators of atmospheric pollution (Rose, 1995), recorded in ponds throughout the lower Mersey region (not presented here) demonstrate that an atmospheric pollution record has been captured.

#### 4. Results and discussion

Down-core  $\chi_{\text{LF}}$ , Pb, S and Zn concentrations for DKC are presented post-1900 with corresponding  $^{210}\text{Pb}$  dates (Fig. 3). Sulphur increases, indicative of coal combustion, from ~1900 to 1944, may reflect a regional signal since the nearest urban centres at this time were Liverpool, Runcorn and Widnes. Potential sources include domestic coal combustion, industrial activities which experienced expansions and diversification during the early 20<sup>th</sup> century, and wartime (WWI: 1914-18; WWII 1939-45) production demands on industries in Runcorn and Widnes, important manufacturing centres in the UK.

There is a clear magnetic, Pb, S and Zn enhancement during the 1960s, corresponding to the establishment of local industries at Halewood, including a car manufacturing plant (opened in 1963). Also, due to urban sprawl during the 1950s and 1960s, Halewood experienced a ten-fold growth in population which may have further impacted air quality. A prominent Zn increase (max: 1164  $\mu\text{g/g}$ , 1963) is observed compared to Pb (max: 333  $\mu\text{g/g}$ , 1970) with subsequent values remaining elevated above pre-1960 levels. It is suggested that industries at Halewood may be an important source of Zn, a metal associated with car plating industries (Graney & Eriksen, 2004). Post-1980 pollution declines may reflect the implementation of air quality legislations limiting for example Pb in air and petrol.

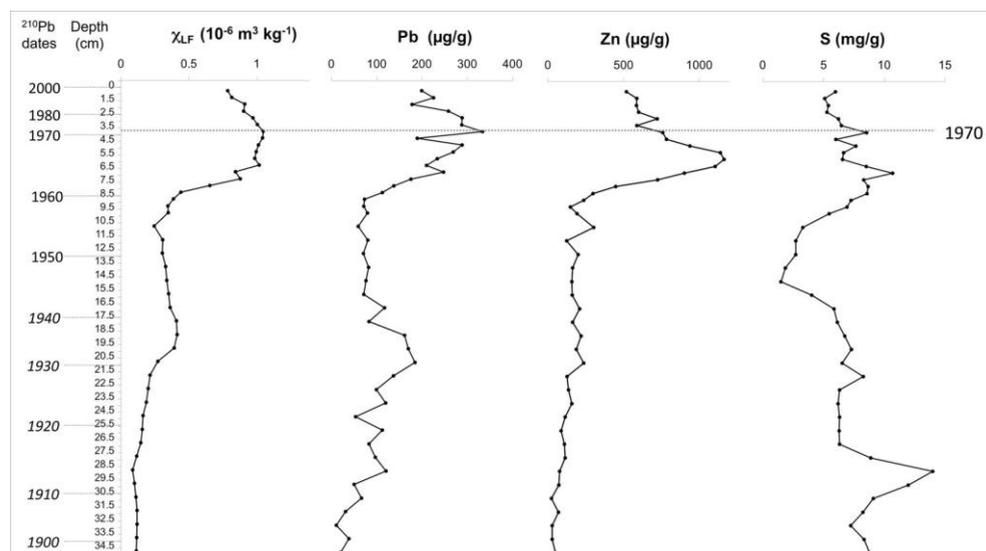


Fig. 3. Down-core concentrations of magnetic susceptibility ( $\chi_{\text{LF}}$ ), lead, zinc and sulphur from Dogs Kennel Clump Pond with corresponding  $^{210}\text{Pb}$  isotope dates (extrapolated dates are italicised). 1970 sediment (highlighted) was selected for further analysis.

Sediment from 1970 was further analysed using SEM-EDS to identify and characterise individual particles from this year. A selection of pollution particles are presented (Fig. 4) and described (Table 2). Spherical particles, indicative of high temperature combustion processes are identified (Fig. 4. A-D) containing Zn, Cr and Sn which may highlight metallurgical sources (Malderen et al., 1996). A vehicle or industrial combustion source may be responsible for particle 'E' which is coated with Pb, providing useful insights into emissions prior to the legislation of Pb in motor fuel and industrial processes. An angular particle rich in Y highlights a non-combustion process, possibly a fugitive industrial dust derived from scrap heaps (Fig. 4 F).

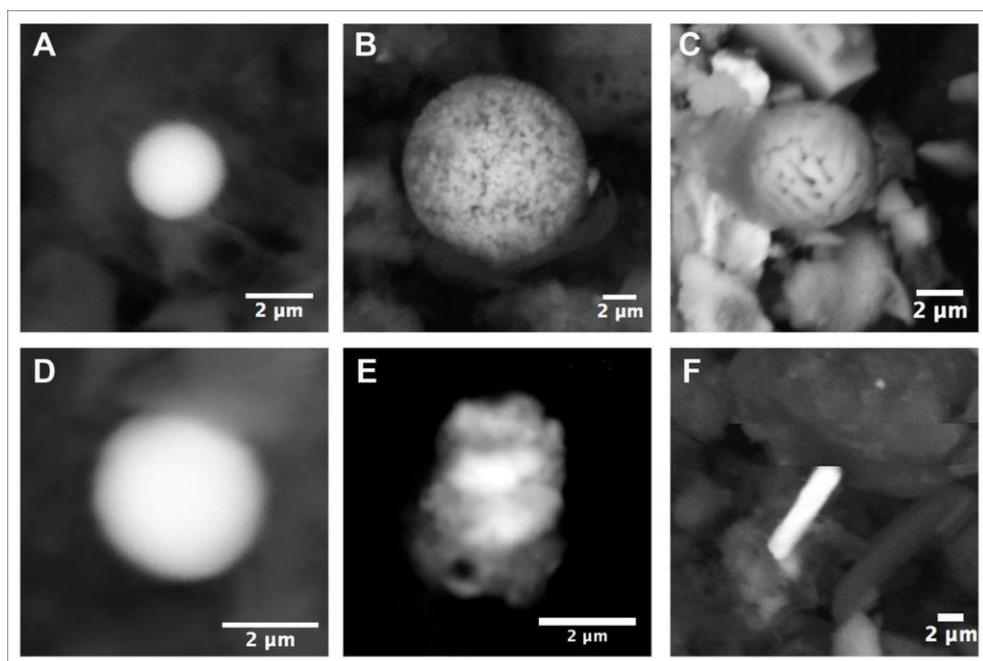


Fig. 4. SEM images of a selection of particles from 1970 preserved in Dogs Kennel Clump Pond.

Table 2: Description of pollution particles from 1970.

Particle	Size ( $\mu\text{m}$ )	Description
A	2.813	Industrial ash sphere comprised of Fe, Si and Sn with smooth surface. Size and Si content suggest a high temperature combustion process. This Sn-rich sphere may indicate fossil fuel combustion, metallurgy or waste incineration.
B	10.954	Mixed metal sphere containing Zn, Ti Cr and Fe. A comparatively coarse particle, combined with the presence of Ti suggests a relatively lower temperature industrial process.
C	5.632	Sphere with high Fe content and skeletal dendritic texture, characteristic of high temperature fly ash (Sharonova et al., 2013).
D	3.562	Aluminium silicate industrial ash sphere with Zn and Cr. Possibly derived from a high temperature metallurgical process.
E	4.282	An aluminium silicate fly ash particle with Pb coating that could be industrial or vehicular- derived. Aperture suggests a cenosphere (hollow particle).
F	8.198 x 1.712	Angular particle containing Yttrium, suggesting a fugitive industrial dust rather than combustion derived. This rare earth element is used in steel alloys and in televisions, highlighting a potential windblown source from scrap heaps in the region.

## 5. Conclusion

Urban sediment archives can be used to rediscover emissions of the past. Down-core trends in pollution proxies from DKC, a pond within a heavily industrialised region, show how the deposition of Pb, Zn and S has varied over time, with trends corresponding to local and regional industrial and urban developments. The pollution record can be explored further by identifying and analysing particulates preserved within sediments of known ages, to allow the size, shape and composition of individual particles to be characterised. Investigating the historical release of pollution particles in this way allows an understanding of how the 'nature' of ambient urban PM has changed over time, and the influence of changing industrial processes, industrial developments/closures, increased road and air travel and the implementation of pollution controls on air quality and toxicity.

This work has important implications for retrospective exposure assessments for urban populations who are most at risk to the harmful effects of urban PM.

## 6. Acknowledgements

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