



Geochemically Based Solutions for Urban Society: London, A Case Study

John Ludden*, Denis Peach, and Dee Flight

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Geochemical data and models can provide a baseline by which to compare changes in the composition of surface waters, groundwater, the atmosphere, soils, and sediments in the coastal megacity of London. The usefulness of geochemical data is dependent on effective communication, which can be challenging. Geochemical tools and approaches can provide evidence to underpin decision making as well as solutions to environmental problems in cities. Geochemists must move beyond simple provision of evidence to describing a solution and then convincing politicians to put this solution into practice.

KEYWORDS: London, geochemistry, soils, water, atmosphere, communicators

INTRODUCTION

As Earth and environmental scientists, our focus is almost exclusively on providing evidence, but not specifically on offering solutions for environmental pollution which require political support. We can provide the boundary conditions (baselines) to a city, such as the weather, river flow, tides, and underlying geology. However, to truly understand the impact of a city on its environment, we must integrate these data with social, engineering, and economic factors in order to provide feasible scientifically based responses to the evidence and to enhance quality of living in megacities. As London (UK) is extremely well monitored and has a history of long-term measurements, we can use London as a scalable case study to examine how a city affects the Earth system. This, of course, includes approaches to de-convolute that impact and get back to a true understanding of what is a baseline and how useful the concept of a baseline might be.

London, which sits on the River Thames, has been settled since early Roman times, and, as such, it bears the legacy of its history and of associated industry and contamination. London clearly demonstrates the concept that cities obey scaling relations with population size, characterizing, as Bettencourt et al. (2007) identified, rates of innovation, wealth creation, patterns of consumption, and human behaviour, as well as the properties of urban infrastructure.

Most cities are continuously growing – a phenomenon known as urbanization – and, as Bettencourt et al. (2007) say, ‘as population grows, major innovation cycles, which refine and redefine the quality of livelihoods, must be generated at a continually accelerating rate to sustain growth and avoid stagnation or collapse’. We can, thus, expect the metropolis of London to continue to grow and prosper. London is a city of ~8.5 million people living in

1570 km² with a gross domestic product of ~£600 billion and, as such, requires continued environmental quality control.

London provides a test case of how a city can live within its landscape. Although ‘urban geochemistry’ (see *Elements*, vol.8, no.6 December 2012) has mainly focused on the problems of environmental pollution, in this article we present some of the issues that are largely a management problem for city planners. We also discuss how we can use information that is based

on a geochemical assessment of London (and other cities) to make living in cities safer, better, and sustainable.

THE IMPORTANCE OF LONG-TERM RECORDS AND THE ROLE OF GEOCHEMISTRY

There are extensive geochemical records, stretching back many decades, on the River Thames and its tributaries; on London’s local atmospheric conditions, soils, and groundwater; and on the Thames Estuary and its sediments. For example, herbage from 1945 to 1990 is stored in Rothamsted Research Station (Harpenden, UK). This stored material acts as a perfect archive of nuclear accident fallout (as from Chernobyl, Russia) from isotopes such as ¹³⁷Cs and ²³⁹Pu, the specific activities of ²⁴⁰Pu (Bq/kg), and of the ratios ²³⁸U/²³⁵U and ²⁴⁰Pu/²³⁹Pu. Research using this archive provided evidence, for the first time, that plutonium contamination originating from America’s Nevada Desert atmospheric weapon tests in 1952 and 1953 extended eastwards as far as north-western Europe (Warneke et al. 2002). As such, this baseline can be used to validate or dismiss claims of local radioactive fallout, such as the alleged nuclear pollution of a wide area around the Royal Air Force Station Greenham Common (Berkshire, UK). While not elaborating on this particular case, the existence of these archives and the ability of geochemists to produce high-quality isotope data proved essential in showing that *local* radioactive fallout was not the cause of the plutonium contamination. This is but one example of the power of defining a baseline composition. Clearly, a city such as London would have several baselines: pre atomic bomb testing, pre industrial revolution, pre large-scale use of nitrate fertilisers, pre extensive use of diesel in vehicles. Environmental impacts, of whatever sort, must be defined relative to appropriate baselines.

The Thames has a record of nitrate concentration measurements that goes back to the mid-19th century (Howden et al. 2011), which is valuable in assessing the long-term nitrate input from agriculture. With 60% of its baseflow coming

* British Geological Survey
Keyworth Nottingham, NG12 5GG, UK
E-mail: jllduden@bgs.ac.uk

from groundwater knowing how the Thames waters are affected by the delayed input from nitrate-containing groundwater aids in our ability to predict future nitrate levels and to meet requirements imposed by governments.

Communicating data analysis, so as not to alarm the population, is a challenge. Moreover, deciding how to impart critical information that may have an impact on the population while at the same time keeping the information in context with respect to norms and measurement uncertainty is not easy. It might be said that communicating the importance and value of our science to non-specialists has become a science in itself.

As stated earlier, geochemists typically provide the evidence and not the solution. They collect data and offer analytical options that can influence a government's policy-making process at all levels. The three examples below show how geochemical knowledge has impacted society and a region's economy, but does not necessarily provide the answers or solutions to the societal problems highlighted by this knowledge.

1. Air pollutants reduce human lifespan in the UK by an average of 8–14 months and by up to 9 years for the most vulnerable groups. In addition, health costs are estimated to be comparable to those of alcohol and drug misuse (COMEAP 2010).
2. Nitrogen pollution costs each person in Europe around £130–£650 (€150–€740) a year (Sutton et al. 2011).
3. The EU Water Framework Directive (2000) assessment of the status of groundwater bodies (Environment Agency 2009) indicated that over 40% were failing to achieve their environmental objectives; 60% of these failures were due to agricultural sources of nitrate. The second largest cause of status failure is pesticides.

London, our case study, is polluted at variable levels and, though the worst polluting activities are now largely past, the pollution itself is still found in the pore waters of London's Chalk aquifer, in river and estuarine sediments, and in local soils. Historic pollutants can be mobilised through bad planning and engineering errors. European norms and similar guidelines need to take account of regional variability and historical pollution. Society today is potentially creating problems for the future with rising levels of aerosol use, rare-element waste products, and a host of unknown effects such as may be produced by the variety of engineered nanoparticles in consumer products that are being increasingly introduced into urban settings.

THE THAMES BASIN

The Thames Basin covers just over 16,000 km² and, with London as the UK's capital at its heart, it is a river basin supporting over 13 million people in a restricted catchment. The River Thames rises from the Jurassic limestone of the Cotswold Hills in Gloucestershire County and flows approximately 235 km to its tidal limit at Teddington Lock in London. At this point, ~60% of the river flow is baseflow (i.e. the amount of water contributed from groundwater systems). Although the UK is considered a wet country, the Thames Basin around London is one of the driest in the country, receiving an average of 690 mm of rain compared to the national average of 897 mm. About 40% of the public water supply in the Thames Basin comes from groundwater derived from the basin's Chalk aquifer, which is its principle aquifer (Environment Agency 2009; Bloomfield et al. 2011)

The geology of London is shown in FIGURE 1. The city is built largely on river terraces, which are underlain by Palaeogene sands and clays (Royse et al. 2012). The Upper Cretaceous Chalk Group (green in the figure) underlies the basin as a whole and has structurally controlled its development. From borehole and geophysical data, the British Geological Survey (BGS) has been able to provide a 3-D reconstruction of the geology (e.g. Aldiss et al. 2012). This geological model is one of the most advanced for any major city. Of particular importance is the detailed reconstruction of the 40–60 m of sediments that overly the Chalk Group: this is critical in defining not only infrastructure, such as rail construction projects and the sewer and drainage systems, but also controlling groundwater flow and pollution pathways in the subsurface and for modern utilities such as the installation of ground-sourced heating systems.

This geological model provides detailed information for ongoing engineering and construction works in London, and the geology also controls the baseline geochemistry of the soils.

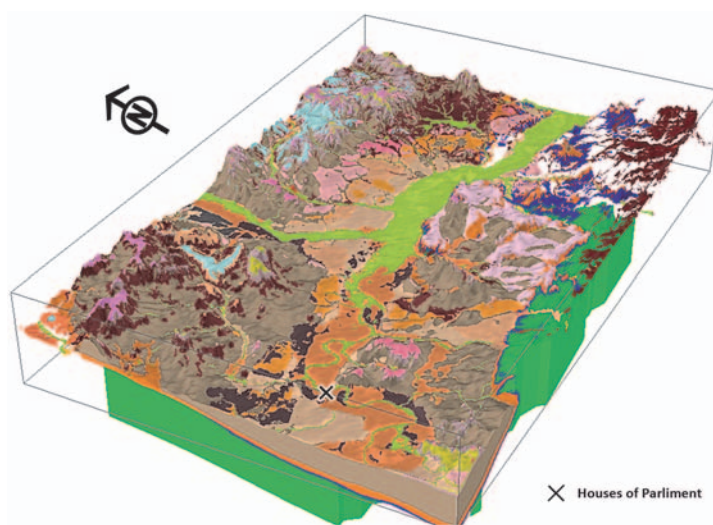


FIGURE 1 Three-dimensional geological map of London (UK) viewed looking from the west across London towards the Thames estuary in the east. For detailed discussion, see Royse et al. (2012) and Mathers et al. (2014). From depth to surface, the Chalk Group (dark green) is overlain by the Thanet Sand Formation (dark blue), the sands, silts and clays of the Lambeth Group (orange), and the London Clay Formation (beige). The other coloured overlayers (pink, yellow, tan, and brown) are various clay and gravel formations and glaciofluvial deposits. REPRODUCED WITH THE PERMISSION OF THE BRITISH GEOLOGICAL SURVEY ©NERC; ALL RIGHTS RESERVED

THE SOILS OF LONDON

The BGS London Earth survey (BGS 2011) collected soil samples at a density of four sites per square kilometre, comprising over 6000 sample sites (sampling density shown in FIG. 2) across the entire London area. At each site, over 50 inorganic chemical elements and properties were measured, a selection of which are now available online (mapapps.bgs.ac.uk/londonearth/londonearth.html). The survey used a systematic and unbiased approach that was independent of land usage or of contaminated sites. This ensured that the survey measured the *baseline geochemistry*, but not necessarily the unmodified original soil compositions. This type of mapping ensured robust results that could be compared to other citywide and national surveys and could, in theory, provide insight into the environmental impacts of urbanization and industrialization, as well as characterizing the geochemical baseline of the UK's most populous city.

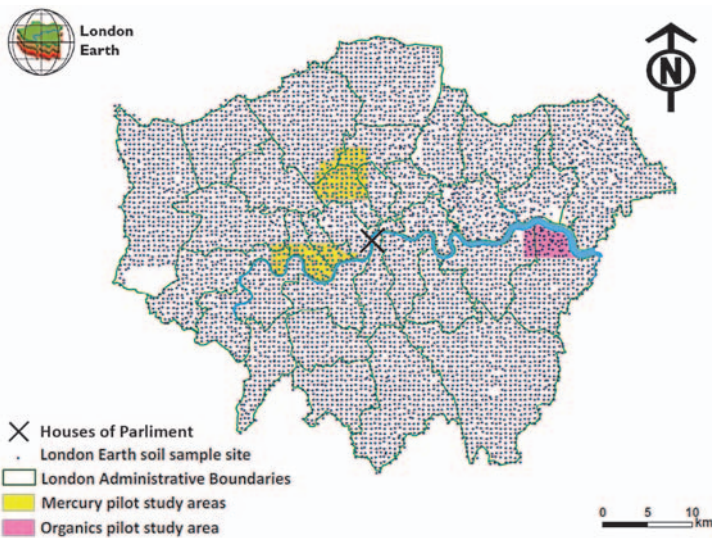


FIGURE 2 Points are locations of top soil samples from the London Earth Project. Pink represents a study area for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (see Vane et al. 2014). Yellow represents a mercury pilot-study area. USED WITH PERMISSION FROM THE BRITISH GEOLOGICAL SURVEY (BGS 2011)

It is possible to deconvolute geological from anthropogenic signals. FIGURE 3 portrays the composite chemistry of silicon, aluminium, and calcium and, if superimposed on the geological model in FIGURE 1, neatly divides the chalk and London clay bedrock and allows identification and quantification of the parent material to the soils. Thus, the 'geogenic' signatures that will dominate rural soil chemistry can also be detected in London's urban region. As described by Appleton et al. (2013), soil parent geology explains ~20–33% of the variance of most elements. Interestingly, it is still quite possible to see that the primary control of the parent rock has not been destroyed even in a major urban centre that has been subjected to intensive urban development, destruction, and redevelopment over many hundreds of years.

The variance of some other elements – including As, Cr, Ba, Pb, Sb, Sn and Zn – is influenced by a mixture of geogenic control (generally <20%) and anthropogenic control (80%). FIGURE 4, for example, shows the distribution of Pb in soils across London. Centrally located highs are focused on high-density population centres and are most likely related to the use of leaded fuel. Other anthropogenic sources are likely to be locally important (e.g. leaded paint); London is ~5 times higher in this latter regard than local rural areas.

As geochemists, we should ask ourselves how our data is used or understood by the general public. As the data are now freely available to the general public and to government and local councils, our biggest challenge is to communicate to the public the meaning of the data we have collected and analysed. Simple messages such as converting units into a form easily understood by the public – '5 mg/kg is equal to 5 grains of sugar in a one kilo bag of sugar' – are important for ensuring public understanding. Equally important is communicating the errors associated with the analyses and averaging processes, and informing the public how elements may be processed by the human body. Geochemists must work with specialists in other fields (e.g. physicians, politicians, media experts) to find the best way to communicate this important information.

London's soil geochemistry data will help to define the background concentration of over 50 elements, including potentially harmful elements such as lead (Pb), arsenic (As),

and nickel (Ni) in soils of the urban and developed areas. In general, geochemists make datasets on the environment available so that individuals, local councils, developers, and organizations can make informed decisions about environmental and health risks (Anders et al. 2013). This information may also prompt local authorities to do follow-up studies.

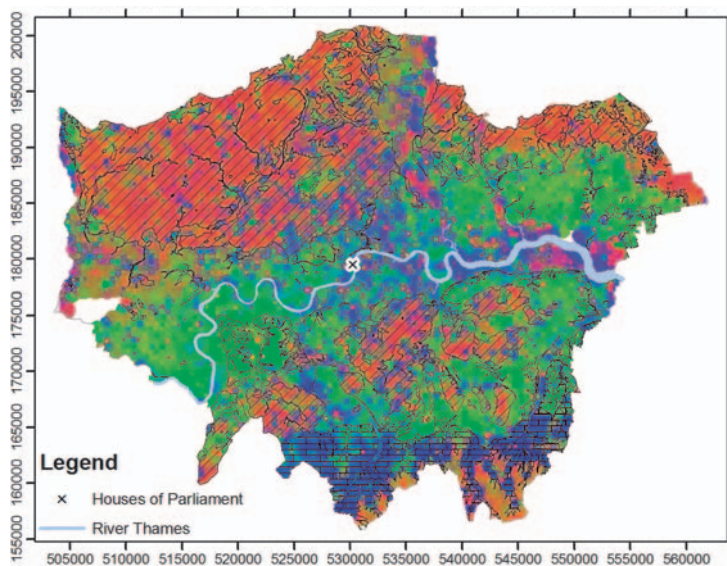


FIGURE 3 London's topsoil geochemistry as taken from the British Geological Survey's Geochemical Baseline Survey of the Environment (G-BASE) project. Regional topsoil samples were collected at a depth of ~5–20 cm with a sampling density of one sample per 2 km² (Johnson et al. 2005). In the London urban area, soil samples were collected from open ground on a 500 m grid at a density of approximately 4 samples per km² (BGS 2011; Flight and Scheib 2011). Sample preparation, analytical methods, and quality control procedures are described in Allen et al. (2011) and Johnson (2011).

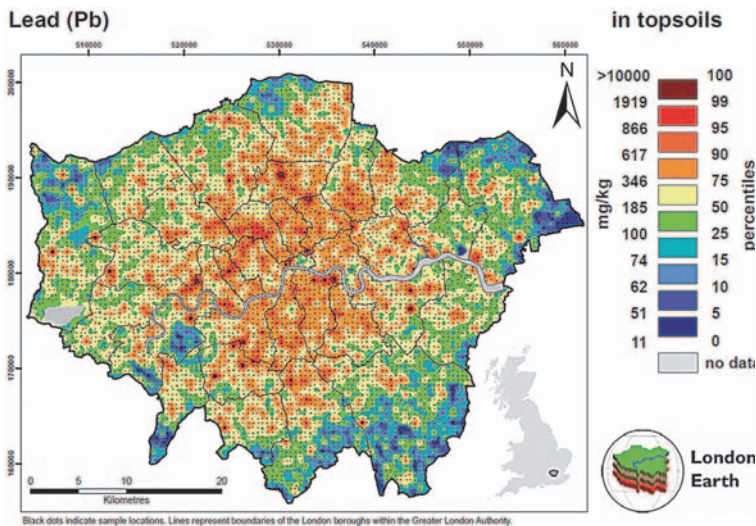
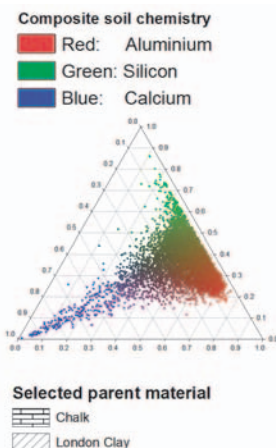


FIGURE 4 Map of lead (Pb) distribution in London's topsoil as taken from the London Earth project.

A significant result of geochemically analysing the soils of London has been simply identifying and locating the polluted areas and pollution pathways, most of which are a legacy of past industrial activities. Hopefully, planners will take this information into account when deciding whether to leave a particular site in its current state (i.e. brown-field), whether to go through with complete site remediation, or whether, for example, to avoid dredging certain parts of the Thames and risk sediment remobilization in estuarine and riverine areas.

NITRATES IN THE RIVER THAMES AND THE 'NITRATE TIME BOMB'

The Thames Basin is in a chalk-dominated catchment area that exemplifies all of the problems pertinent to groundwater, including groundwater flooding and contamination issues. Nitrate concentrations for the Thames River at Hampton have records dating back to 1868 (Howden et al. 2011). These form the basis for modelling nitrate export from the Thames Basin and offer some interesting observations, e.g. nitrate export was 50 kg ha^{-1} prior to WWII but has now tripled, as shown in FIGURE 5A, in post-war years because of the increased use of fertilizers.

High nitrate in water is an economic and human health problem that often leads to water eutrophication. High-nitrate concentrations in drinking water may also reduce the ability of human blood to carry oxygen and,

in the very young, may cause 'blue baby syndrome' (Bryan 2006). The costs of nitrate treatment for the UK water industry rose from £16 million (\$25 million) per year in 2000 to £58 million (\$90 million) per year in 2005 (DEFRA 2006). The domestic and industrial water supplies to London comes from the river and groundwater. In dry weather and droughts, all the water in the river originates from groundwater. However, the river water may have been used and recycled (e.g. treated sewage effluent) several times on its journey from the Cotswold Hills through Oxford and Reading and into London.

Given that the Thames has a strong groundwater influence, remediation of the river depends on the rate of nitrate removal through biological and physical processes in the groundwater system. This is shown in FIGURE 5B where the nitrate input function is described. The black dots show individual pore-water nitrate concentrations from 300 cored boreholes in the BGS database. These concentrations have been back-plotted to give nitrate concentrations at the base of the soil zone at their year of recharge, which has been calculated using depth in the profile and the estimated undersaturated zone travel time of peak nitrate. The red solid line shows nitrate input spans derived from literature data; the blue crosses show average nitrate concentration for a given year calculated from the pore-water data. The nitrogen application rates ($25\text{--}70 \text{ kg N ha}^{-1} \text{ y}^{-1}$) indicated in FIGURE 5B reflect the historic different levels of industrialization and the introduction of measures to reduce the fertilizer application rate.

Wang et al. (2012) define the nitrate concentrations in groundwater as a 'nitrate time bomb' that could affect not just London but the UK as a whole. They describe a simple process-based geographical information system (GIS) model that simulates nitrate transport in the unsaturated zone of rock and soil and that predicts the arrival time for peak nitrate loading for the UK's water table. This GIS model links the nitrate input function (the temporally varying but spatially uniform leaching of nitrate from the base of the soil) to the factors of unsaturated zone thickness and lithological dependence rate of nitrate transport through the saturated zone and so makes an estimate of the arrival time of nitrate at the water table.

Restoring surface nitrate concentrations in the London region to values typical of the pre-intensification period (i.e. pre-1940s) would require massive basin-wide changes in land use and management approaches that would compromise food security and take decades to be effective. This is clearly not practical. However, groundwater modelling and understanding nitrate baselines will be essential to inform future policy decisions on London's long-term land management and water use.

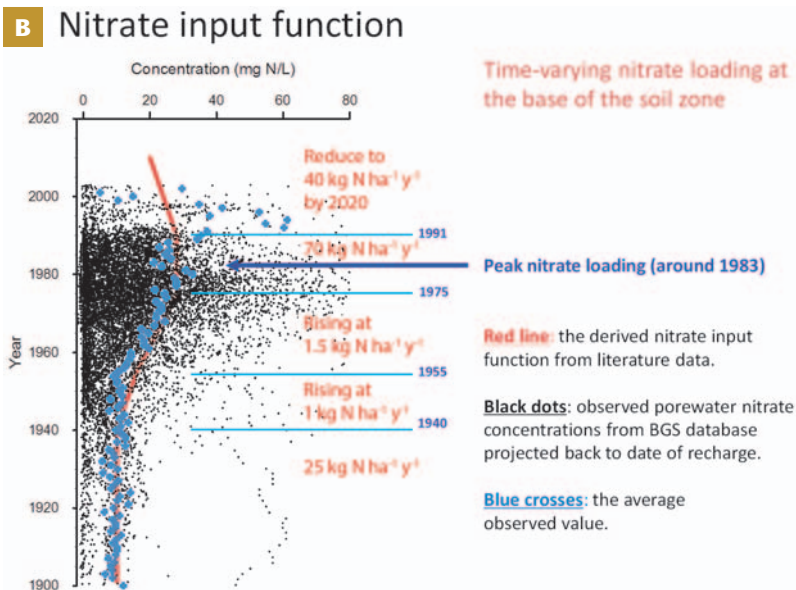
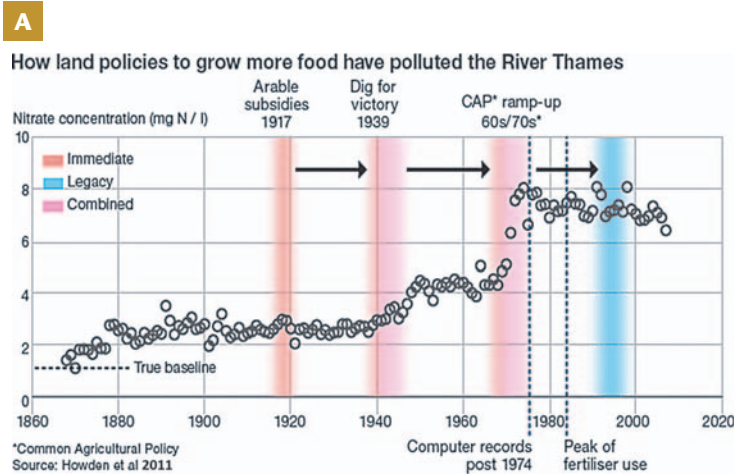


FIGURE 5 (A) Nitrate concentrations in the River Thames as measured at Teddington Lock since 1868 (Howden et al. 2011) showing how land policies over the last 100 years have impacted on pollution levels. (B) Application of nitrogen fertilizers increased from pre-WWII rates of $25 \text{ kg N ha}^{-1} \text{ y}^{-1}$ to $\sim 70 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in the early 1980's. Nitrate levels (black dots) in groundwater from 300 wells across the UK reflect this increase as shown by the nitrate input function (red line) and average observed levels (blue crosses). Wang et al. (2012) estimate that peak nitrate levels have not been reached in the water table, suggesting a future 'nitrate time bomb' that will negatively impact groundwater quality.

ATMOSPHERIC POLLUTION IN LONDON (THE CLEARFLO EXPERIMENT)

Atmospheric conditions in London, in contrast to legacy problems derived from polluted soils and river sediments, depend in part on the current use of fuels and on present industrial processes. And, these atmospheric problems are increasingly in the public eye. For example, on 5 March 2015, the *London Evening Standard* ran the following article: 'Toxic London: Shock Figures Show That We're Breathing the Filthiest Air in Britain? Top Pollution Hotspots are Marylebone and Park Lane From Park Lane to East Ham, the City's Air is Filthy'. This headline was based on high NO₂ levels that had arisen due to a temperature inversion. People are concerned as they see and feel this as a direct effect on their health.

To monitor and react to London's potentially poor air conditions, the ClearfLo experiment (Clean Air for London) was set up (www.clearflo.ac.uk). This was designed to provide long-term integrated measurements of the meteorology, composition, and particulate loading of London's urban atmosphere. Measurements were made at street level and at elevated sites, complemented by modelling to improve predictions for air quality. This experiment took place during the winter of 2012 and during the London summer Olympics.

For the first time in London, or any major city, the ClearfLo experiment aimed to:

1. Establish an infrastructure to measure meteorological conditions, gaseous composition, and particulate loading
2. Determine the meteorological processes that control London's urban boundary layer; the atmosphere in which most of the planet's population now lives
3. Determine the chemical processes that control the concentrations of ozone (O₃) and NO₂
4. Determine the chemical and physical processes that control the size distribution and chemical composition of particulate matter and identify its sources
5. Evaluate the strengths and weaknesses of air quality models

The ClearfLo monitoring and measuring infrastructure was installed at multiple heights above the ground surface: from street level to tower tops. The data collected, analogous to the soil/sediment geochemical data, allowed the identification of what was urban background and what was an anomaly. The measurements were complemented by numerical atmospheric simulations.

The first results from ClearfLo were described by Lee et al. (2014) and Bohnenstengel et al. (2015). FIGURE 6 summarises a model, centred on London, of mean NO_x concentrations gridded at 12.5 m above ground and compared for winter and summer periods. This model emphasises the vertical structure and evolution of the urban boundary layer and incorporates the chemical controls on atmospheric NO_x and O₃, in particular the composition and role of particulate matter. The model results clearly define the seasonality of London's air quality and also confirm the poor atmospheric conditions of the city.

DISCUSSION: WHAT IMPACT ARE WE MAKING?

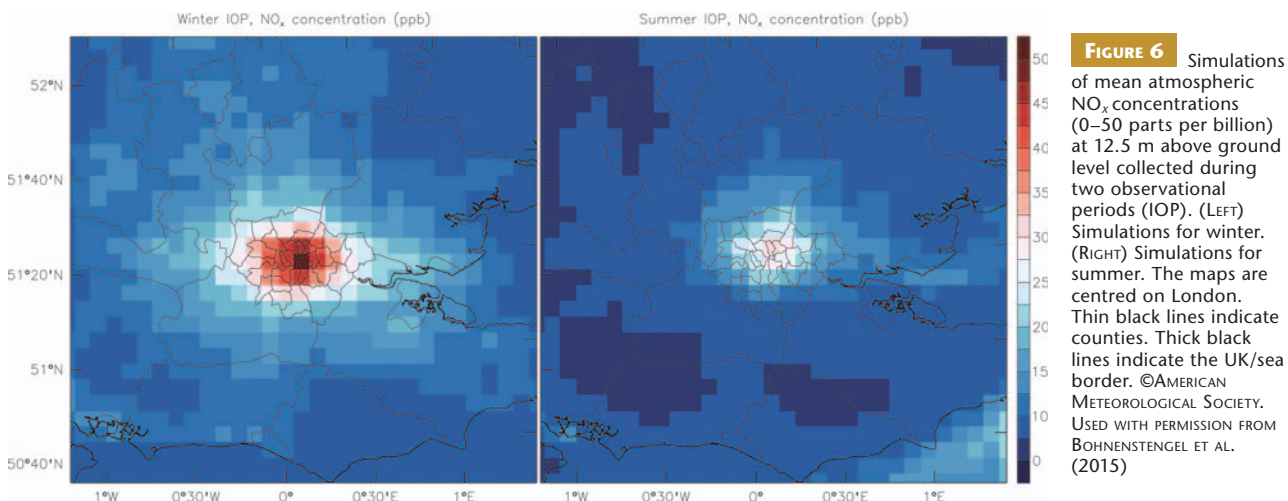
In a previous issue of *Elements* that focused on urban geochemistry, Wong et al. (2012) neatly laid out the challenges for urban space. These included dealing with atmospheric pollution, waste management (discharge and landfill), runoff (roadway, surface and greenspace), infrastructure failures (sewage, subway seepage), and groundwater and heat abstraction. In this article, we have addressed some of the problems described by Wong et al. (2012) by highlighting current work on London's soils (the London Earth project), its hydrology and geohydrology (the so-called 'nitrogen time bomb'), and its atmospheric contaminants (the ClearfLo project).

Urban areas are increasingly a platform for scientific research and require us, as scientists, to move from our own evidence-gathering to working with other specialists so as to provide robust solutions to the problems involved with biodiversity and conservation, contaminated land studies, urban-rural land-use planning, and how contaminated environments affect human health.

We must establish real-time monitoring systems that are carefully placed at arm's length from government and the commercial world. Monitoring should be transparent, and authoritative data should be used to reassure the public that we are able to 'whistle blow' and, when needed, force authorities to intervene, remediate, or shut down operations, however commercial or critical. Yet at the same time, we must educate the stakeholders who will want to interpret the geochemical data.

We know that our cities are polluted. Legacy issues, for example, indicate the following:

1. The worst is largely past, but the pollution is still present in the groundwater, in river and estuarine sediments, and in the soils from where it can be mobilised through bad planning and engineering errors.



- European (and other) norms need to take account of regional variability and historical pollution and modelling studies, such as that indicated for the 'nitrate time bomb'.
- That we may be creating new and ongoing problems with aerosols, nanoparticles of rare elements and other critical metals and of unknowns.

CONCLUSIONS

London provides an excellent test case by which to examine a wide range of urban geochemistry that, in one way or another, affects the lives of those living there. It is environmental scientists who define the boundary conditions to life in this or any city. However, we do not provide solutions to any problems arising. Is it possible for us to work with the social and economic sectors and build models on how best to *live with* the city and understand the feedback mechanisms between work, play, and the city?

Can we use geochemical and other environmental data to build impact into infrastructure models, financial models, population models, ecological models, and water and air quality models? To an extent, some of the legacy issues are best identified and then left untouched (placing a virtual

'Do Not Disturb' sign on some of the metal pollutants in sediments in estuaries and rivers), although communicating the risks of managing these hazards to the public and town-planners is a major challenge.

London, and cities like it, will grow and evolve, and environmental scientists will need to rise to that challenge to make sure our cities remain places where people and businesses can thrive. Given the wealth of environmental information in the London urban area, can we now model the environmental impact of the city on its catchment area and then scale this to other cities around the world? If so, we could develop a best practice for managing the legacy of centuries of environmental damage in any city.

ACKNOWLEDGMENTS

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