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The use of electrochemical sensors for monitoring urban air quality in low-cost, high-density networks

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HIGHLIGHTS

► Suitably configured electrochemical sensors can be used for air quality studies.
► Evidence of performance of electrochemical sensors at parts-per-billion levels.
► Sensors are sensitive, low noise, highly linear and generally highly selective.
► Measurement density (space and time) unachievable using current methods.
► Show low-cost air quality sensor networks are now feasible for widespread use.

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ABSTRACT

Measurements at appropriate spatial and temporal scales are essential for understanding and monitoring spatially heterogeneous environments with complex and highly variable emission sources, such as in urban areas. However, the costs and complexity of conventional air quality measurement methods means that measurement networks are generally extremely sparse. In this paper we show that miniature, low-cost electrochemical gas sensors, traditionally used for sensing at parts-per-million (ppm) mixing ratios can, when suitably configured and operated, be used for parts-per-billion (ppb) level studies for gases relevant to urban air quality. Sensor nodes, in this case consisting of multiple individual electrochemical sensors, can be low-cost and highly portable, thus allowing the deployment of scalable high-density air quality sensor networks at fine spatial and temporal scales, and in both static and mobile configurations.

In this paper we provide evidence for the performance of electrochemical sensors at the parts-per-billion level, and then outline results obtained from deployments of networks of sensor nodes in both an autonomous, high-density, static network in the wider Cambridge (UK) area, and as mobile networks for quantification of personal exposure. Examples are presented of measurements obtained with both highly portable devices held by pedestrians and cyclists, and static devices attached to street furniture. The widely varying mixing ratios reported by this study confirm that the urban environment cannot be fully characterised using sparse, static networks, and that measurement networks with higher resolution (both spatially and temporally) are required to quantify air quality at the scales which are present in the urban environment. We conclude that the instruments described here, and the low-cost/high-density measurement philosophy which underpins it, have the potential to provide a far more complete assessment of the high-granularity air quality structure generally observed in the urban environment, and could ultimately be used for quantification of human exposure as well as for monitoring and legislative purposes.

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1. Introduction

1.1. Air quality and human health

Studies have shown that human health and urban air pollution, in the forms of both gas-phase species and particulate matter, are closely linked (e.g. World Health Organisation, 2000). In terms of gas-phase pollutants, nitrogen dioxide (NO_2) is identified as a key species that can affect quality of life and mortality rates (e.g. World Health Organisation, 2006). Both NO_2 and carbon monoxide (CO) are known to be respiratory sensitisers (e.g. McConnell et al., 2010) and both have a proportionally greater effect on those with existing respiratory or cardiovascular conditions (e.g. HEI, 2010). Long-term exposure to NO_2 also adversely affects lung function, whilst CO reduces the body's capacity to transport oxygen, thus affecting cognitive function at lower concentrations and being toxic at elevated concentrations (Lehr, 1970; Abelsohn et al., 2002). While seemingly not of primary importance for direct health impacts, nitric oxide (NO) rapidly interconverts to NO_2 (via reaction with ozone (O_3)) and, through its influence on the tropospheric O_3 budget, affects the oxidising potential of the troposphere. While clearly of obvious significance for health, legislation and atmospheric science, particulate matter is not discussed further here.

1.2. Existing measurement networks

In the UK, the largest network of sensors routinely monitoring gas-phase pollutants is the Automatic Urban and Rural Network (AURN) which is operated by the UK Department for Environment Food and Rural Affairs (Defra), with 132 monitoring sites currently in operation (Defra, 2011). The UK AURN is designed primarily to monitor NO_2, NO_x, CO, O_3, SO_2 and particulate matter (PM_{10} and $PM_{2.5}$).

Monitoring is also routinely undertaken in many parts of the world, including Europe and North America (e.g. the Environment Canada National Air Pollution Surveillance program which has 286 sites (Environment Canada, 2011)). In some areas of the world, however, information on air quality is either highly sparse (tending to be localised around a particular city or institute) or completely non-existent.

The costs of setting up fixed site monitoring stations using traditional technologies can be substantial, with individual instruments costing between £5000 and £60,000, and with significant additional resources required for maintenance and calibration (e.g. Ropkins and Colvile, 2000). Operation of such sites is also constrained by the need for significant infrastructure (secure enclosures, mains power etc.). The consequence is that, while well proven in terms of precision and accuracy of air quality measurements, most existing networks are sparse as higher network densities would be impractical as well as prohibitively expensive. There is, therefore, an urgent need to complement existing air quality monitoring methodologies with flexible and affordable alternatives, to improve monitoring capabilities for both scientific and legislative purposes, to allow source attribution and to improve understanding of health impacts of urban air quality.

Alternatives to existing high-cost sparse fixed-site monitoring stations have been discussed previously by several groups. For example Kamionka et al. (2006) discuss the potential of low cost sensors to increase measurement spatial resolution thereby complementing existing relatively sparse fixed sites. While they argued that measurements needed not necessarily to be at the accuracies or precision possible with traditional in situ instruments, they were not able to demonstrate suitable instrumentation. Low-cost alternatives for use at typical ambient concentrations have been investigated by for example De Vito et al. (2008) and Carotta et al. (2001), however these were primarily based on metal-oxide chemo-resistive sensors, as industrial electrochemical sensors had up to then not been developed with sufficient sensitivity for use in low-ppb regimes. The use of low cost sensors within networks has also been investigated (e.g. Tsujita et al., 2005), albeit with a lower spatial density and sensitivity than those described in this work. Collectively, these works highlight the difficulties in making measurements in the highly spatially variable and complex urban environment. The need for selectivity and stability in sensors for monitoring low concentrations in complex gas mixtures in the urban environment is illustrated in for example Pijolat et al. (1999) and Kamionka et al., with the potential for increasing measurement density in urban centres being also discussed by De Vito et al. (2008, 2009), based on the same sensor methodology as Kamionka et al. Although not discussed in this paper, both De Vito et al., and Tsujita et al., stressed the importance of calibration of urban air quality sensors in the reduction of measurement error, whilst Carotta et al., described the need for careful control of the sensor manufacturing process in ensuring sensor repeatability. This paper builds on elements of this previous work, demonstrating performance of state of the art electrochemical sensors at the parts-per-billion level.

While acknowledging the importance of particulate matter in air quality, this paper focuses on the capability of electrochemical sensors for gas-phase measurements (in this case NO, NO_2 and CO) and the demonstration of sensor networks utilising such techniques. The longer-term ambition is to extend the low-cost, high-density sensor network philosophy not only to other gas-phase species, but also to particulate matter and local micro-meteorology as suitable technologies become available.

2. Electrochemical sensors

2.1. Principle of operation

The electrochemical sensors used for these studies are low-power, robust and low-cost, and are based on widely understood amperometric sensor methodologies designed for sensing selected toxic gases at the parts-per-million-level in the industrial environment. Many detailed descriptions of amperometric sensing methodologies are available in the literature, and so only a brief overview is given here.

Each sensor contains a cell which incorporates three electrodes separated by so-called wetting filters. These filters are hydrophilic separators which enable ionic contact between the electrodes by allowing transport of the electrolyte via capillary action. The electrodes are termed the working, reference and counter electrodes (see Fig. 1). The working electrode is the site for either reduction or

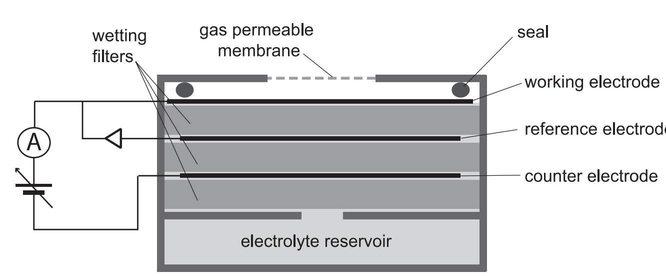

Fig. 1. Schematic of an electrochemical cell of the type used in this study. The gas diffusion barrier is a gas-permeable PTFE membrane used to prevent water and dust ingress to the cell. During operation the working and counter electrodes are maintained with a fixed voltage bias, and the current between them is the output of the sensor.