Distributed Environmental Monitoring

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Abstract With increasingly ubiquitous use of web-based technologies in society today, autonomous sensor networks represent the future in large-scale information acquisition for applications ranging from environmental monitoring to in vivo sensing. This chapter presents a range of on-going projects with an emphasis on environmental sensing; relevant literature pertaining to sensor networks is reviewed, validated sensing applications are described and the contribution of high-resolution temporal data to better decision-making is discussed.

Keywords Air, Chemical sensors, Environmental monitoring, Sensor networks, Water

Contents

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Abbreviations

μFIA	Micro-flow injection analysis
μTAS	Miniaturised total analysis system
ANN	Artificial neural network
DCU	Dublin City University
EPA	Environmental Protection Agency
FET	Field-effect transistor
GC	Gas chromatography
GHG	Greenhouse gas(es)
GPRS	General packet radio service
GSM	Global system for mobile communications
ICT	Information and communication technology
IR	Infra-red
ISE	Ion selective electrode
LED	Light emitting diode
LOD	Limit of detection
MS	Mass spectroscopy
OEJT	Organic electrochemical junction transistors
PEDD	Paired emitter detector diodes
SC-ISE	Solid contact ion selective electrode
UME	Ultra miniature electrode
VOC	Volatile organic compound
WFD	Water framework directive
WSN	Wireless sensor network

1 Introduction

The past decade has witnessed a dramatic upsurge in activity and commercial interest in the area of wireless sensor networks (WSNs). This is understandable given the availability of infrastructure capable of providing a functioning communications backbone for these devices. This infrastructure has already had enormous impact on society, with people becoming accustomed to instantaneous access to a wide range of information through mobile phones, laptops and digital TV screens. This in turn has given rise to new industries providing services that have profoundly changed how we function as individuals and how we collectively function as a society. In order to survive, major industry players seek to predict where the next big opportunity will come from, in order to position themselves in this space as early as possible before the rapid growth phase begins. However, in a world wherein the dynamic of change is itself accelerating and financial uncertainties increase risk, predicting the next big win has become critical for the future stability of many companies. Given this context, it is unsurprising how many of these major corporations are predicting the emergence of WSNs as the next big opportunity for the ICT (information and communication technologies) sector. For example, Hewlett Packard's visionary strategy [1] for globally connected sensor networks envisages heterogeneous sensor networks monitoring a multitude of parameters and feeding this information to the "cloud" from where a host of service-based applications can be realized. HP's Thought Leader Peter Hartwell captures the excitement of the scale of the opportunity, albeit somewhat sensationally; "one trillion nanoscale sensors and actuators will need the equivalent of 1,000 internets: the next huge demand for computing!" Predictions from companies like INTEL, IBM and Nokia lead to the same conclusion, with Nokia presenting a very convincing case for sensor networks in its strategic vision for sensor networks (the Nokia visionary video "Morph" is a conceptual graphic summary of what could happen over the coming decade as nanotechnology-based sensing technologies and communications technologies begin to merge the molecular and digital worlds [2]). Hence there is a driving force from major industry players to develop the basic building blocks of WSNs, i.e., sensors with integrated communications capabilities [3]. It has been envisaged that WSN developments will involve a "top-down" emergence of sensor nodes [4]. Under such a strategy, initial activity would focus on relatively sophisticated systems that would fully meet the criteria of the sensing operation though having associated drawbacks in terms of expense and power consumption; once established, the focus would shift to more densely distributed lower-cost and lower-power intensive nodes, albeit with lower functionality. Indeed these two levels of node complexity can co-exist as two distinct layers of sensing capability, where the simpler and more expansively deployed nodes can be used to adjust the operating characteristics of the less densely distributed but more sophisticated devices (e.g., wake up, increase sample rate), thus circumventing the limitations arising from expense and power consumption. The interaction between two layers of sensor networks with different levels of complexity enables the respective advantages of dense distribution (yielding extensive temporal and spatial data) and sophisticated capability (involving high accuracy and reliability) to be capitalized upon, thus allowing what has been termed "adaptive monitoring" [5–7].

Our specific interest in sensor networks is related to the integration of chemical sensors and biosensors (autonomous instruments that provide information about the molecular world) into sensor networks [4, 8]. In particular, we seek to identify and overcome the obstacles that inhibit the full realization of widely deployed chemo/bio-sensors in sensor networks [5]. The WSN literature is predominantly concerned with sensors that target physical parameters such as temperature, pressure, movement, vibration, light level, sound and such like. This is understandable, as these sensors tend to be low-cost, rugged, durable and reliable, maintain calibration over time and consume little power. Such characteristics are essential for the massive scale-up implicit in the WSN concept, as articulated above. In contrast, chemo/biosensors are expensive to buy and maintain, are unreliable in autonomous operation, do not maintain calibration, have limited lifetime and consume considerable power [9]. Our research focuses on understanding the factors underlying these very considerable obstacles, and identifying strategies through which they may be overcome [10].

Conventionally, chemical sensing begins in the laboratory under strictly controlled conditions, which often involves the addition of chemical species that ideally reacts selectively with a target analyte and subsequently changes in some measurable property that is proportional to the concentration of the target analyte; many such examples exist in the literature [11–14]. More importantly to the context presented here are practical examples of such chemical sensing capabilities. In this contribution, we shall describe several sensing platforms that can provide remote access to information arising from the molecular world of chemistry and biology, and illustrate their use in several on-going environmental deployments. Sections 2 and 3 shall discuss sensing technologies pertaining to gas and water quality monitoring, respectively, with case studies provided to illustrate on-going collaboration with relevant agencies and industrial partners. These efforts in environmental monitoring endeavour to develop sophisticated sensor nodes with a view to advancing to ubiquitous sensor nodes' deployment—such networks would provide the flexibility, scope and comprehensiveness that simply cannot be achieved from currently employed manual spot measurement techniques. The ability to monitor air/water quality is essential for maintaining quality—this is exemplified by the finding by Bernhardt et al. [15] that the effectiveness of $14–15bn on river restoration projects in the USA between 1990 and 2005 is not fully known. Autonomous sensor networks featuring large-scale, dense distribution of sensor nodes necessitate very low-cost sensor nodes with adequate reliability and longevity. Such challenges are sought to be overcome by electrochemical sensors; the potential of such sensors is outlined in Sect. 4. Section 5 outlines the end-to-end acquisition and meaningful analysis of data collected from WSNs. An example of an air quality monitoring dataset is analyzed to illustrate the reasoning that can be derived from such data and how it can be conducive to better informed decision-making based on observed events. In the course of such discussion, we will demonstrate how even limited scale deployments of these emerging technologies can give rise to entirely new information accessible through web databases to industry, enforcement bodies, government agencies and the general public alike.

2 Gas Sensing: Autonomous Systems for Air Quality Monitoring

2.1 Introduction

Numerous motivations exist for gas detection: pollution minimization to reduce emissions that adversely affect local ecosystem as well as having potential global implications; human risk mitigation in the form of characterizing toxic and/or odorant gases; and gas handling diagnosis, where the unintentional leaking of gases from industrial plants and transfer pipes holds financial loss ramifications, in addition to posing a risk with regard to flammable or toxic gases. The impact of industrially generated gas emissions on the environment has prevailed in the world media in recent years [16, 17]. The significance of this has been further reinforced with the formation of international legislation to quantify and subsequently reduce harmful emissions [18]. The emphasis of such international efforts and media attentions has been targeted at the so-called *greenhouse gases* (GHG): carbon dioxide (CO_2) and methane (CH_4) gases have been identified as contributors to the greenhouse effect [19], which has been linked to climate change through modification of the insulating properties of Earth's atmosphere. In addition to their contribution to the greenhouse effects on a global scale, gas emissions can be detrimental to their local environment. CO_2 poses an asphyxiation risk as it is denser than air [20], while excessive CH_4 levels results in the death of surrounding vegetation [21]. Sulphur dioxide (SO_2) and mono-nitrogen oxides (NO_x), principally arising from internal combustion in automotive vehicles [22], produce acid rain from reactions with oxygen and water vapour to form sulphuric acid (H_2SO_4) and nitric acid (HNO_3), respectively [23]. Furthermore, SO_2 is contributory to the formation of smog in cities [24] while nitric oxide (NO) leads to excess nitrogen in water, affecting water quality and consuming oxygen content to kill fish stocks [25]. Other examples of toxic gases are carbon monoxide (CO), hydrogen sulphide (H_2S) and volatile organic compounds (VOCs). In addition to these toxins, ammonia (NH_3) and methane (CH_4) are unpleasant odorants, with CH_4 also posing a significant fire hazard when existing in the highly flammable range of 5–15% v/v in air [26].

The use of autonomous sensor networks can effectively fulfil the sensing requirements of the aforementioned target gases, especially concerning remote monitoring in inaccessible areas and long-term continuous acquisition. Such acquisition would enable the characterization of trends in defining the dynamics of the target gas generation and migration. This is demonstrated in the following sections, where an overview of the predominant sensor devices is outlined. Furthermore, these technologies are discussed in the context of developed autonomous gas monitoring applications.

2.2 Gas Sensing Technologies

In selecting the sensor technologies to fit to a specific application, the most prevalent criterion tends to be the minimization of sensor cost. Gas sensors tend to be dominant proportion of overall cost of the monitoring device, thus the employment of low-cost sensors would serve to reduce the annual cost of routine air quality monitoring. In 2000, this expenditure was estimated to be in the region of €320,000 per year in Ireland, excluding special studies and research aspects [27]. With greater industrialization and the substantial increase in the volume of vehicular traffic since then, the cost of air monitoring today has undoubtedly increased substantially in excess of this figure. Other general criteria for sensor selection are power consumption and gas selectivity. Low power consumption is advantageous for low operational costs and extended time deployments. Gas selectivity is application dependent, where a high sensitivity for the target gas is desirable to prevent interference with other gases present in the sample. The context of autonomous sensor networks introduces a number of other criteria, driving the need for compact and rapid acquisition devices. Traditionally, gas sensing involved the capturing of an air sample either via bagging or absorption on an applicable chemical surface. This sample is subsequently processed in a laboratory, using methods such as gas chromatography (GC), mass spectroscopy (MS) and infrared spectroscopy [28, 29]. Such techniques have been used by the UK and USA environmental protection agencies, whereby two methods are employed: the chamber method and the tracer flux method [30–32]. The chamber method involves a volume of gas being collected on-site using a sealed gas-tight enclosure, with the sample being transported to a remote laboratory for analysis, e.g., by GC–MS. The tracer flux method involves the controlled release of a tracer gas (selected to be readily distinguishable from the target gas) at specific locations in the landfill, with samples being grabbed at locations downwind to monitor the plume dispersion [26]. The effectiveness of both methods has been reported to be comparable [33]. While these techniques yield very accurate results, the laborious process and substantial time delay between acquisition and results (typically spanning several days) would not be suitable for critical events where a rapid detection and alerting would avert a potential catastrophe. The predominant sensor technologies employed to enable portable, real-time measurements include semiconductor, pellistor, ionization, electrochemical, infrared and colorimetric sensors.

Semiconductor sensors work on the principle that the sensor material (comprised of one or more metal oxides) varies its electrical resistance depending on the absorption of the target gas [34]. When no gas is present, the sensor resistance returns to its default condition. Amongst other applications, these types of sensors have been developed to measure NH_3 with reasonably fast response times [35], SO_2 [36] and gas compositions in catalytic convertors in car exhausts [37]. One of the principle drawbacks of this type of sensor is its susceptibility to poisoning [38], i.e., the metal oxide materials become unresponsive after reactions with certain types of gases, thus incapacitating the sensor. Furthermore, the behaviour of these sensors is dependent on sample temperature and humidity as well as requiring the presence of oxygen to function [39], hence limiting its range of applicability for WSNs.

Pellistor sensors detect gases that have a significantly different thermal conductivity to that of air [40, 41]. Heating elements incorporated into the sensor ignite the target gas; the generated heat produces a change in resistance in the catalyst-loaded ceramic detecting elements. Since the target gas needs to be ignited, the selectivity of the device is limited to combustible gases only. Furthermore, regular maintenance is required and measurements can become unreliable over time [42]. As with semiconductor sensors, poisoning is a possibility and the presence of oxygen is required for proper functioning. These limitations signify that pellistor sensors are not particularly suited to WSNs.

There are two types of ionization detectors: flame-ionization and photo-ionization. The ionization of the target gas results in a change in electrical charge output, which is read as the sensor measurement [43]. The two methods differ by their means of ionization: flame-ionization employs a hydrogen-air flame to produce the ions [44] while photo-ionization involves the gas being bombarded with high-energy photons (typically from the UV spectrum) [45]. These methods are effective at sensing organic compounds and VOCs, though the flame-ionization method is limited to combustible gases. Furthermore, flame-ionization has a disadvantage in that it is a destructive detection method, thus not preserving the sample. Ionization methods involve expensive (ca. $2,500) and complex devices, thus not being viable as a basis for a large-scale network of nodes required for WSNs.

The operation of electrochemical sensors is based on the oxidation or reduction reaction that occurs between the target gas and device electrodes [46]. Redox electrodes often employ amperometry, in which the electrodes are poised at a certain potential at which it is known the target gas can be oxidized or reduced, and the resulting current is proportional to the concentration; more sophisticated sensors use voltammetry in which the electrode voltage is varied and the resulting voltammogram used to quantify the concentration. The latter technique is predominantly used for aqueous samples rather than gas sensing applications. These sensors feature very low limits of detection in the region of parts-per-billion [47–50]. Electrochemical sensors have very small power consumption, an ideal feature when considering autonomous sensor networks. However, these sensors tend to have limited functional lifetime—like the other sensors based on an active surface, they tend to be poisoned or lose sensitivity as the surface composition changes over time in real environments. In addition, these sensors can experience interference from other gases [51]. Furthermore, the sensors' performance is quite sensitive to temperature, requiring internal temperature compensation and thermal stability in the sample [52]. Electrochemical sensors have been used to successfully detect NO [47], NO_2 [48, 52], H_2S [49] and SO_2 [50]. Developmental work in the area of electrochemical sensing is discussed in greater detail in Sect. 4.

Infrared (IR) sensors are typically used to detect hydrocarbons, toxic and combustible gases, with limited sensitivity for VOCs [53]. The sensor is comprised of an IR radiation emitter and detector pair, wherein a specific portion of the IR bandwidth is absorbed based on the molecular vibrations of the target analyte. The detector is tuned to specific characteristic bands for each target gases, e.g., 2,360 cm^{-1} for the O=C=O stretch in CO_2 [54] and 3,017 cm^{-1} for the C–H stretch in CH_4 [55]. The extent of the IR wavelength absorption, as identified by the detector, indicates the concentration of the target gas in the sample. These types of sensors have excellent selectivity, range (up to 100% v/v with resolution in the region of parts per million), rapid response time and immunity to poisoning. Such characteristics are advantageous for WSNs; however, these features result in the sensors being quite expensive and power intensive. The presence of water vapour in the gas sample can also affect the IR sensing capabilities due to the airborne moisture absorbing IR radiation, thus potentially masking the presence of the target gas in humid environments [56].

Colorimetric sensors involve the characterization of a colour change arising from the reaction between the target gas and chemically sensitive colorimetric layer [57, 58]. While the sensing surface is susceptible to changes that are not due to interactions with the target (e.g., surface fouling, dye photobleaching), these sensors show promise in terms of very low-cost devices, particularly when coupled with colour measurement approaches such as optical fibre transducers [59] and paired emitter detector diodes (PEDD) [60, 61]. Recent research has been concerned with optimizing colorimetic sensors in terms of achieving stable, reversible reactions with a distinct colour difference between protonated and deprotonated states of the colorimetric states [60–64]. Such research has indicated positive results for sensing CO_2 and NH_3.

Gas sensing studies such as those by Shepherd et al. have demonstrated a WSN set-up within an environmental sensing chamber and showed the ability to detect and track the movement of chemical plumes in gas form [57]. This study allowed for an intermediate step before real deployments where the dynamics of a plumes movement could be studied and modelled [65] and thereby allowing for a more comprehensive understanding of chemical plume movement and detector placement. Fraser et al. [66] developed a sensor system for detecting airborne contaminants such as ammonia concentrations via the response of coated piezoelectric crystals. Similarly, Klinkhachorn et al. [67] have implemented a chemical sensing system with five piezoelectric quartz crystals for the detection of chemical spills in hazardous waste sites. Furthermore, the work by Barko et al. [68] has developed a chemical sensor array using this approach but applied the use of Artificial Neural Networks (ANNs) and showed a promising way of differentiating and identifying between volatile compounds (acetone, benzene, chloroform and pentane). Another gas-based study based on sensor networks has been conducted by Becher et al. [69] where they employed metal oxide gas sensors for the detection of a multitude of evaporating hazardous materials including: organic solvents NO_2, O_3, CH_4, CO, H_2S, NH_3 along with other pollutants in air. Similar work was reported by Somov et al. [70] with more of a focus on the sensing infrastructure and methane detection. In addition, Fay et al. have placed multiple systems capable of detecting greenhouse gas emissions from landfill sites for a period of ca. 3 years [71] that were relatively low in cost compared to others. For instance, a study by Karellas et al. [72] monitored air pollution emissions from a fire started at a factory in Guelph, Ontario who manufactures chemicals for use in swimming pools. The technology employed here was a mobile vehicle capable of monitoring hydrogen chloride and chlorine gas emissions from the factory in real time; however, the cost base for such an approach is not feasible for widespread detection systems. Furthermore, a project known as “PROTECT” in the USA was launched where a number of chemo/bio-sensing systems were installed in Penn and Grand Central railway stations with each unit costing ca. $25,000 and a maintenance cost of $1.7 million over 3 years [73, 74]. Clearly, more widespread deployments of this kind would be prohibitively expensive. The key to progress is therefore the realization of lower cost, yet reliable, chemical sensing platforms that will form the basis of much larger scale deployments.

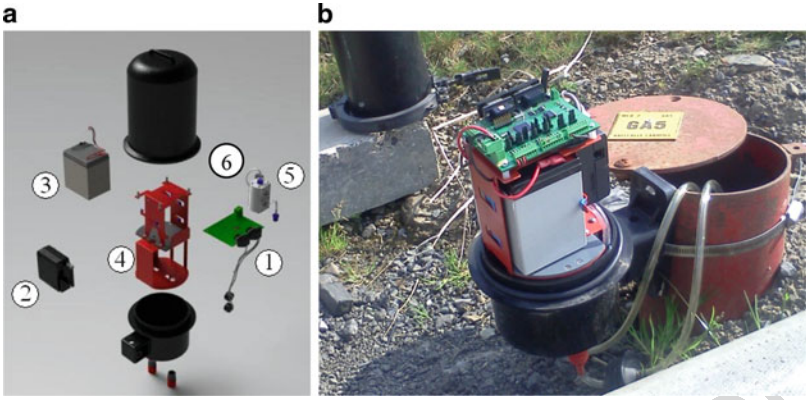

Fig. 1 Developed autonomous landfill gas monitoring platform, (**a**) exploded view, (**b**) as deployed on borehole well. (*1*) control board, (*2*) GSM module, (*3*) battery, (*4*) extraction pump, (*5*) sample chamber and sensors, (*6*) protective casing

2.3 *Gas Sensing Application Case Studies*

In recent years, Diamond and co-workers [71, 75, 76] have been involved in the development of autonomous platforms for the real-time monitoring of gases in the environment. Current applications include the monitoring of GHG and odorant gases, specifically CO_2 and CH_4 produced from the anaerobic decomposition of waste at landfill sites. Such monitoring is relevant to the mandatory licencing terms of landfill sites, as regulated by the Environmental Protection Agency (EPA). Infrared gas sensors (sourced from Dynament Ltd., UK) were chosen for this application due to their range of detection, rapid response time and poisoning immunity being best suited to the unpredictable composition and transient fluctuations associated with landfill gas emissions. The compact and rugged construction of the platform, shown in Fig. 1, permits the platform to endure long-term deployment in inhospitable environments with continually successful operation [71, 75, 77].

To date, extensive field deployment trials have been conducted at sites collaboratively selected with the Office of Environment Enforcement (OEE), the regulatory division of the EPA. Systems were fitted to borehole wells located at the landfill perimeter to permit monitoring of any gas migration. Key deployments include two continuous monitoring durations in excess of 12 months (March 2010 to March 2011): an active landfill site spanning 364 days/8,736 h in duration with 1,148 data points collected; and a dormant site spanning 371 days/8,904 h, with 1,255 data points collected. The full dataset from the active site, an operational landfill located in the north-east of Ireland, is shown in Fig. 2.

Over the deployment duration, it can be seen that the measurements of CO_2 regularly exceeded the threshold level of 1.5% v/v as stipulated by the EPA. Measurements of CH_4 in excess of the threshold level of 1% v/v were more intermittent; however, recurrent peaks can be observed that posed a particular concern when occupying the 5–15% v/v flammable range of CH_4 in air. Such

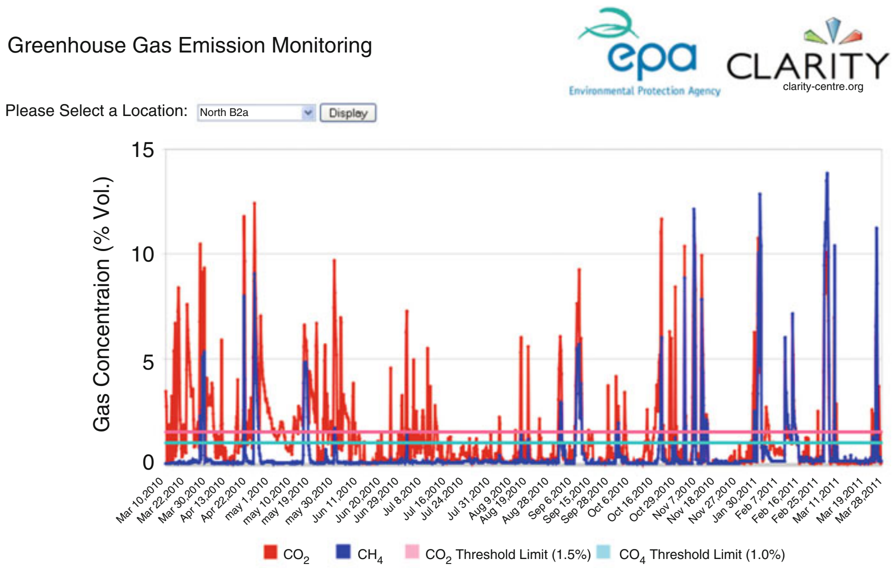

Fig. 2 Field data for a 12-month deployment on an active landfill site

high-rate temporal data afforded by the autonomous systems has hitherto been unavailable to enforcement agencies and site management; research is now underway to attribute the gas generation and migration effects to causes such as weather factors, landfill structure modification and extraction system effectiveness.

Further scope of such devices has been affirmed by the EPA and a number of other interested parties with interest in the monitoring of hazardous pollutants and toxins, including but not limited to NO_x, CO and H_2S. The modular design of the platform allowed for sensors to be interchanged, broadening the number of potential applications for this device. Such a platform had been developed as a pilot trial for the passive (i.e., sample not pumped) monitoring of carbon monoxide. Electrochemical sensors (Nemototech, Italy) were deemed to be a better choice for this application due to low cost and low power consumption. The autonomous platform was deployed at the exit to a multi-storey car park on DCU campus. An excerpt of the data collected from this deployment is shown in Fig. 3. A number of events are clearly identifiable, as annotated on the graph. Event “a” occurs between 5 and 6 pm during the working week (Mon to Sat) when most people leave the DCU campus. Event “b” corresponds to patrons after a show at the local theatre.

2.4 Conclusions

Cost, power consumption and selectivity form the basis for establishing a gas sensing network. Regardless of the nature or location of the sensing application,

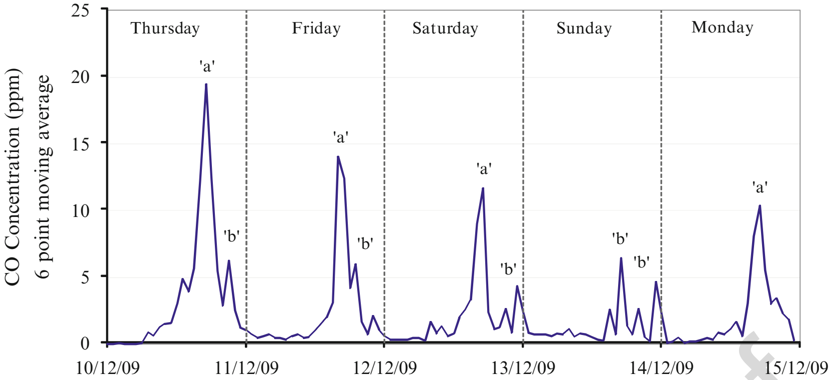

Fig. 3 Carbon monoxide monitoring in multi-storey car park

the remote data acquisition from IR or electrochemical sensors via an onboard microcontroller and communication using GSM (or, where applicable, radio protocols such as GPRS, ZigBee, etc.) enables the appropriate information to be transmitted to a central base station. From here, a representation of the statistically significant data is uploaded onto a secured online database, allowing a concise and intelligible visualization of the monitored data for the relevant authorities and stakeholders, as demonstrated in Fig. 2. In this way, a fully autonomous sensor node is realized and the value of its monitored data is validated. Current work is ongoing in the deployment of multiple systems on a single landfill site to form an integrated sensor network. This work represents a pioneering effort in monitoring landfill gas in Ireland, whereby distributed sensing platforms will provide increased temporal and spatial data. The web-based monitoring enables the site operators and EPA to characterize, for the first time, the transient nature of landfill gas migration in a real-time and fully autonomous process; this new information can in turn assist in the development of more effective management procedures, and control of the underlying processes that govern greenhouse gas emissions from such sites.

3 Water Sensing: Reagent-Based Systems Using Optical Detection for Water Monitoring

3.1 Introduction

There is a growing need for increased monitoring of natural waters and wastewaters that is being motivated by significant legislative and societal drivers. To ensure that the quality of water bodies (including rivers, lakes, groundwater, coastal waters and the oceans) is protected, data on a large and growing range of chemical species are required. Moreover, this data needs to be available at a higher temporal and geographic resolution than is achievable using traditional water-monitoring practices, which have been dominated by manual sample collection followed by laboratory analysis using a range of techniques. While this approach, properly implemented, can provide high-quality data, it is expensive due to the high manpower requirements and in some cases the high cost of analysis, and the sampling frequency is consequently typically quite limited. There is, therefore, a need for portable, robust, accurate water monitoring systems which can be used to measure water quality in situ at relatively high frequency over extended deployment times.

Since the "miniaturized total analysis system" (μTAS) concept was introduced by Manz et al. in 1990 [78], microfluidic or "lab-on-a-chip" technology has been seen to offer a range of properties which make it suitable for the development of compact, autonomous analytical devices. In this context, the advantages of microfluidic sensing systems can be summarized as (1) small flow rates used, typically in the $\mu L\ min^{-1}$ range, which minimize sample size, reagent consumption and waste generation, (2) small size, facilitating the development of compact and portable analytical systems, (3) speed of analysis derived from performing chemical analysis on the μm scale, where diffusion-based mixing can be an efficient process and (4) potential for low-cost devices. This combination of properties makes microfluidic systems highly attractive as a basis for reagent-based monitoring of chemical species in the aquatic environment.

There are, however, also drawbacks associated with operating at the micro-scale; the small samples sizes have implications in terms of properly representing the complete body of water which is to be measured, while the small size of the channels and other features of micro-analytical systems means that they are susceptible to blockage or interference by even fine particulate matter. The former issue can be mitigated by the higher measurement frequency which is possible using in situ systems, while the use of fine filters at the sampling point can minimize the latter issue, although at the cost of limiting the analytical parameter to the dissolved fraction of the target species. Nevertheless, issues such as these and others, including interference caused by bubble formation/trapping within the analytical system, have represented significant barriers to the development of truly successful microfluidics-based in situ sensing systems. Although numerous and frequently highly sophisticated micro-analytical systems have been developed and assessed under laboratory conditions, examples of integrated micro-analytical devices which have been successfully deployed for extended periods under real environmental conditions are much scarcer. While the development of sensing nodes for the aquatic environment which are sufficiently reliable and low in cost to form the basis of extensive WSNs has been anticipated, realization of this goal has been more difficult to achieve. The challenges to developing such systems include stability and reliability of the analytical system, cost and power consumption of the integrated device, robustness in harsh environmental conditions and fouling due to particulate matter and microorganisms. In developing an autonomous environmental monitoring device, deployable lifetimes on the order of months to years are desirable, depending on the specific application. Achieving such lifetimes without elevating the fabrication cost of the integrated system to unviable levels can be described as the key challenge for developers. In this section, we focus on integrated microfluidics-based systems for water quality monitoring applications.

3.2 *Microfluidic-Based Water Monitoring Technologies*

As the fabrication of microfluidic systems has been reviewed elsewhere [79, 80], we will mention this topic only briefly. A wide variety of materials and techniques have been used for the fabrication of microfluidic analytical systems. Some of the most commonly used materials include silicon, glass, and polymers such as poly (dimethylsiloxane) (PDMS), poly(methylmethacrylate) (PMMA) and polycarbonate. Depending on the material, application, and size and aspect ratio of features required, fabrication techniques including photolithography, soft lithography, micro-milling, injection moulding and embossing have been used to form microfluidic chips with a range of components such as channels, mixers, separators, integrated detectors, valves and pumps.

An area which has seen significant progress is the integration of colorimetric methods for nutrients such as phosphate, ammonia and nitrate/nitrite into microfluidic manifolds with LED/photodiode-based optical detection systems. Worsfold and co-workers developed a miniaturized, LED-based chemical analyzer for in situ monitoring of nitrate [81]. The limit of detection (LOD) with a 20 mm path length flow cell was 2.8 mg L^{-1}. The linear range was adjustable to suit local conditions in the field by changing the flow cell path length and/or sample loop volume. The analyzer was used in shipboard mode for mapping nitrate concentration in the North Sea and in submersible mode for a transect of Tamar Estuary (UK). Doku and Haswell [82] developed a micro-flow injection analysis (μFIA) technique for orthophosphate based on the molybdenum blue reaction. The μFIA manifold was formed by etching of borosilicate glass, and electro-osmotic flow was used both for the mobilization of reagents and for sample injection. An LOD of 0.1 μg mL^{-1} was achieved, with a rapid analysis time of 60 s and low sample/reagent volume (total system volume of 0.6 μL). Greenway et al. [83] produced a similar μFIA system for the determination of nitrite, based on the Greiss reaction to form an azo dye. Following optimization of the electro-osmotic flow characteristics, reaction chemistry, and injection time, an LOD of 0.2 μmol L^{-1} was achieved. A further progression of this work [84] was to incorporate a cadmium reductor column within the device to use the same method for the analysis of nitrate in water, producing an LOD of 0.51 μmol L^{-1}. Daridon et al. [85] investigated the Berthelot reaction for the determination of ammonia in water utilizing a microfluidic device consisting of a silicon chip between two glass plates. The pathlength in this device was 400 μm, and the integrated system comprised fibre optics coupled to an LED. High aspect ratio channels (30 μm wide × 220 μm deep) were used for sample/reagent mixing in order to achieve efficient diffusional mixing.

Azzarro et al. [86] described an automatic colorimetric analyzer prototype (MicroMAC FAST MP3) for high frequency measurement of nutrients in seawater. This system utilizes the Berthelot method for ammonia detection, the sulphanilamide/ethylendiamine method for nitrate detection, and the blue phosphomolybdate method for phosphate detection, and LODs of 5, 2.5 and

2.5 μg L^{-1} were reported for $N\text{-}NH_4$, $N\text{-}NO_3$ and $P\text{-}PO_4$, respectively. The system is based on loop flow analysis technology developed by Systea, an Italian company, and has been further developed to provide a system more suited to deployment on typical monitoring platforms [87]. This multi-nutrient analyzer system has been trialled in collaboration with YSI Hydrodata at two locations in the UK (Hannigfield Reservoir and River Blackwater Estuary) [88].

Other systems for in situ nutrient monitoring have been field tested by the Alliance for Coastal Technologies (ACT), Chesapeake Biological Laboratory, Maryland, USA [89–91]. The American Ecotech NUT 1000 was originally developed by Monash University and commercialized by Ecotech Pty. Ltd. The system can achieve LODs for reactive phosphate of <3 μg L^{-1} with a response time of 30 s. The high sampling rate is due to the use of rapid sequenced reagent injection in combination with a multi-reflection flow cell. Reagent injection also minimizes the reagent consumption, allowing over 1,000 measurements to be performed with only 20 mL of reagent. In the ACT trials, the NUT 1000 (which is non-submersible) was used for surface mapping onboard a research vessel in Monterey Bay, California [90]. Very good correlation with validation samples was achieved, after correction for a measurement offset of 50 μg L^{-1} P-PO4, which was attributed to differences in refractive index of natural seawater versus the reagent grade water used for preparation of internal standards and machine calibration. The ACT has also reported on successful deployments of the WET Labs Cycle-P nutrient analyzer [91] and the YSI 9600 Nitrate Monitor [89].

Vuillemin et al. [92] described a miniaturized chemical analyser (CHEMINI) for dissolved iron and total sulphide, based on FIA and colorimetric analysis. Designed for deep-sea applications, the system is submersible to a depth of 6,000 m, with detection limits of 0.3 μM and 0.1 μM for iron and sulphide, respectively. It has been used to document the chemical environment prevailing within mussel beds, performing 8 assays/day over a 6-month deployment period.

Koch et al. [93] presented the individual microfluidic instrument components to be used for an integrated micro-total-analysis device for in situ, colorimetric, water quality monitoring. Components include a microfabricated filter, a passive micromixer, a 1-cm pathlength microfluidic absorbance flow cell, mini-motor-driven peristaltic micropumps, a miniature collapsible reagent storage bag, and compact water-proof packaging.

Sieben and co-workers [94, 95] developed a stand-alone sensor platform with integrated sub-systems, which is portable and capable of in situ reagent-based nutrient analysis. The system is based on a continuous flow, microfluidic absorption cell and a low cost optical detection method, together with an automated microfluidic delivery. The system was characterized using the Griess reaction for detection of nitrite, achieving an LOD of 14 nM. The platform can also be configured to detect a range of parameters including nitrate, phosphate, iron and manganese using appropriate colorimetric chemistries. In the nitrite-detection configuration, the system was deployed at Southampton Dock and operated in situ for 37 h, performing 284 discrete measurements.

Reagent stability is often a major limitation when considering methods for environmental monitoring. Devices ideally need to be left in the field for a significant period of time and give reproducible results during this time frame. Sequeira et al. [96] addressed the stability of the reagents for the Berthelot reaction for long-term monitoring applications. The three key reagents in the reaction are potassium sodium tartrate, phenol and hypochlorite. While potassium sodium tartrate and phenol are generally regarded as stable if stored properly, hypochlorite solutions are commonly unstable and typically decompose to form chlorate ion and oxygen over a period of days or weeks. It was shown that ensuring that the hypochlorite solution was free from contamination with Fe and Cu, which catalyze the decomposition, allowed long-term stable storage of the hypochlorite solution. Salicylate was also used as a replacement for phenol and was found to yield broadly similar analytical performance in terms of the sensitivity, and kinetics, while having the major advantages of being highly stable and non-toxic. Bowden et al. [97, 98] evaluated the vanadomolybdophosphoric acid method (yellow method) as an analytical method for the determination of phosphorus in water within a microfluidic device using stopped flow with the aim of producing an automated device with a field lifetime of 1 year. In this method ammonium molybdate, $(NH_4)_6Mo_7O_{24}.7H_2O$, is reacted with ammonium metavanadate, NH_4VO_3, under acidic conditions. The combined reagent and sample containing orthophosphate react to form the vanadomolybdophosphoric acid complex, $(NH_4)_3PO_4NH_4VO_3.16MoO_3$. The resulting solution has a distinct yellow colour arising from the strong absorbance of this complex below 400 nm. It was shown that batches of the reagent could be used for over 1 year with no significant loss in performance [98]. This method was therefore selected in preference to the molybdenum blue method, due to the greater stability of the reagents used in the analysis, and resulted in an assay with an LOD of 0.2 mg L^{-1} and a dynamic linear range of 0–50 mg L^{-1} (Fig. 4). AU2

The importance of water-based chemical sensing has been highlighted by driving forces such as the Water Framework Directive (WFD) [99] and review articles outlining the need for reliable analytical methods for monitoring chemical pollutants [100]. Examples of deployments reported within the literature include one by Wang et al. [101] where electrochemical sensors were employed in the detection of pH (potentiometric) and nitrate (amperometric). In addition, the work by Yang and Ong et al. [102, 103] has deployed a network of magnetoelastic sensors for the detection of pH in drinking water. Zhu et al. describes a system capable of remotely monitoring parameters such as pH and dissolved oxygen in a fish farm culture site [104]. Another study carried out by Capella et al. has reported the ability to measure nitrate, ammonium and chloride within Lake Albufera, Valencia, Spain, by means of ion-selective electrodes (ISEs) distributed and communicated in an in-line fashion [105]. In addition, recent works by Okoliša have been reported the creation of integrated WSNs for the measurement of several chemical species in water and wastewater [106]. Other contributions have been described by Ilyas/Mahgoub [107] and Buffle/Horvai [108]. Although there are many other examples within the literature, the ultimate driving force and implementation of such a sensing infrastructure must be driven on a national level. For

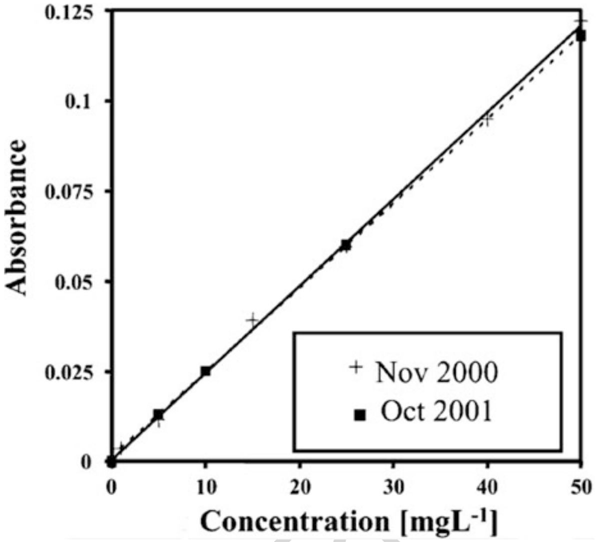

Fig. 4 Calibration comparison demonstrating long-term chemical stability of the yellow (vanadomolybdophosphoric acid) method. Reproduced with permission from [98]

example, in Ireland, challenges exist in this area for Irish governmental agencies and a key example includes the "DEPLOY" project by O'Flynn et al. examining a 2-year deployment of 5 sensor stations along the length of a river in Ireland capable of continuously measuring parameters such as pH, conductivity, turbidity, dissolved oxygen amongst others with an aim to address the demands of the WFD [109].

3.3 Water Monitoring Application Case Studies

Diamond and co-workers [110–112] have developed a prototype autonomous integrated microfluidic analyzer based on this method whose performance has been validated in field trials in wastewater and natural waters. More recently, a substantial redesign has yielded a second generation system with similar analytical specifications but with significant improvements in the areas of size and portability, ease of deployment, deployable lifetime and fabrication cost. The current phosphate analyzer, shown in Fig. 5, is designed to autonomously sample, analyze and communicate data for long periods of time in remote locations. Power is supplied by a 3.6 V lithium battery. Sample is drawn into the system through a 0.45 μm filter membrane. Reagent, high standard solutions and low standard solutions are stored in PVC bags. A waste bag is also used to collect all waste generated by the system. Fluid handling is performed using three dual channels peristaltic pump heads driven by geared electric motors. One channel of each pump head pumps reagent while the other pumps the sample, high standard solution or low standard solution. The dual channel set-up minimizes the effect of pump outflow pulsation, an inherent property of peristaltic pump set-ups. The pump outlets are connected directly to the

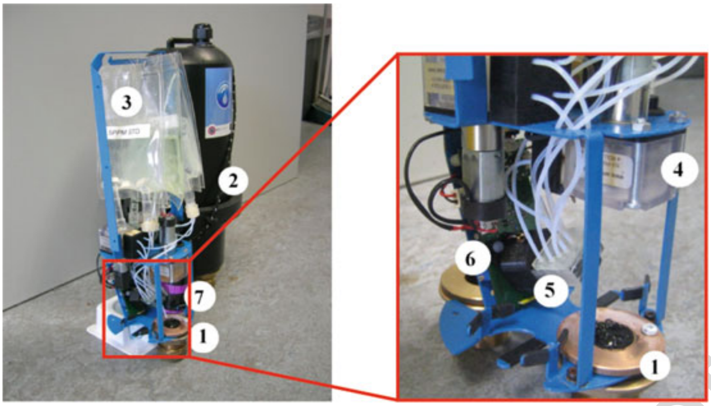

Fig. 5 Nutrient analyzer design (*1*) sample inlet, (*2*) IP68 enclosure, (*3*) PVC bags, (*4*) dual channel pump head, (*5*) microfluidic chip, (*6*) electronic control board, (*7*) battery

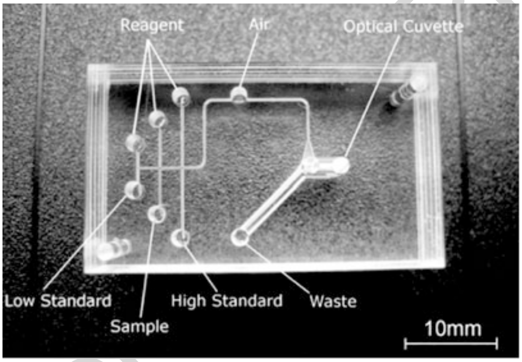

Fig. 6 Microfluidic chip design

microfluidic chip. The seven inlet/single outlet microfluidic chip can be seen in Fig. 6. An air inlet is also supplied to the chip. An air pump is used to flush the chip after each reaction cycle. The air flush reduces the effect of sample carry over and is also used to flush the chip on occasions when air bubbles interfere with the light path in the detector area.

The optical detection system takes an absorbance measurement on the reacted sample through the microfluidic chip optical cuvette. The detection system consists of an ultra violet (ca. 380 nm) LED and photodiode. A Texas instruments MSP430 microcontroller controls all system operations. Measurement data is stored locally on flash memory and also broadcast wirelessly using either short range ZigBee radio or GSM to a network gateway or base station. The complete system is housed in an IP68 rated compact enclosure (dimensions approx. 130 mm diameter by 320 mm height).

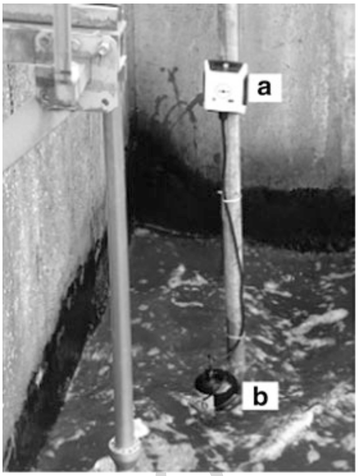

Fig. 7 The phosphate sensor in situ during a trial at a wastewater treatment plant. (*a*) Sensor unit. (*b*) Communications unit

In a recent trial of the second generation phosphate sensor, the system was deployed at a wastewater treatment plant in Co. Kildare, Ireland. The sensor was used to monitor the phosphate levels in the plant's treated effluent directly prior to discharge. The system was mounted as shown in Fig. 7, with the sensor unit directly immersed in the effluent while the communication unit was raised approx. 1 m above the water level to ensure reliable communications were achieved.

An autosampler with refrigerated storage capability was installed adjacent to the effluent tank and used to collect 24 samples per week for validation purposes. These samples were analyzed in the laboratory using the vanadomolybdophosphoric acid method. Data from the trial is shown in Fig. 8, which shows that the sensor and sample readings were generally in good agreement. The unusually high levels of phosphate in the effluent near the start of the trial period were due to a failure of the plant's tertiary treatment system based on ferric chloride dosing to remove phosphate by coagulation. After this system was restored to operation a gradual decrease in phosphate level was observed. Thereafter, the phosphate levels were generally in the 2–3 mg L^{-1} range. Sensor readings were not obtained from 21/05/2011 to 24/05/2011 due to an unusually low water level in the effluent tank, which meant that sample was not accessible to the sensor.

3.4 Conclusions

A range of deployable microfluidic systems for reagent-based optical detection of various water quality parameters have been developed and deployed with varying degrees of success. Significant barriers to the broader uptake of these systems still exist, while these vary depending on the individual system and application in question, they can be summarized as (1) limited deployable lifetime due to factors such as reagent stability or storage capacity, power consumption or susceptibility to biofouling,

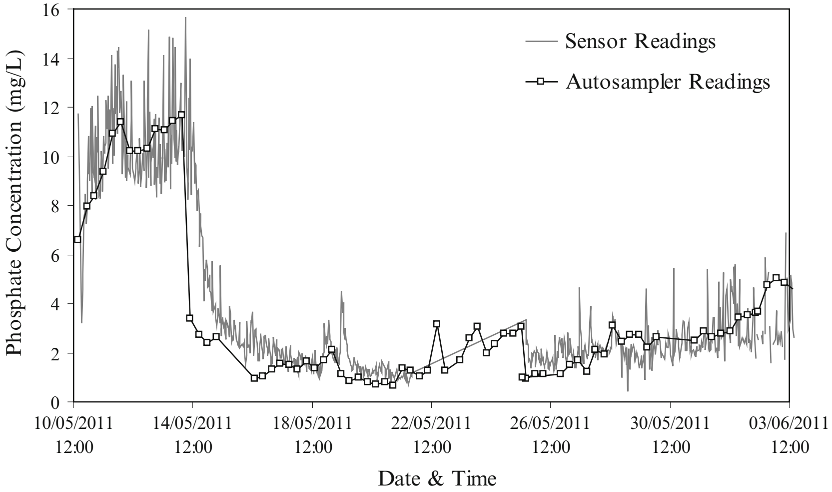

Fig. 8 Data from a trial of the 2nd generation phosphate sensor

(2) relatively high cost of manufacture/operation, (3) reluctance on the part of end-users to move away from well-characterized and standardized laboratory methods. The key to overcoming these barriers is the development of low-cost systems which can operate reliably for extended deployment periods without the need for regular maintenance. The phosphate analyzer system described here has achieved significant steps towards the achievement of this goal, and long-term validation trials are ongoing with the aim of demonstrating the reliability of the data which can be collected by this system over longer deployment periods. Ongoing work is also focussed on implementing detection methods for other analytes of interest with the platform provided by the phosphate analyzer, while future plans include the integration of other novel components, such as detectors based on paired LEDs [113, 114] and a low-power conductive polymer-based microfluidic pump [115].

4 Electrochemical Sensing: Potential and Challenges of Using Electrochemical Methods in Remote Autonomous Instruments

4.1 Introduction

There are a numerous publications on electrochemical sensors in the literature [116–125] due to their low potential cost and their compatibility with conventional mass production [118, 126, 127]. Electrochemical sensors have advantages over optical ones related to situations wherein the use of reactive dyes may have issues related to stability, toxicity and cost [123] or is precluded, for example, in strongly coloured or turbid samples [122, 124], or in cases for which no appropriate dye exists. Moreover, the combination of different sensor types can offer complimentary information allowing the extraction of a richer set of data [118]. Presently, screen printing appears to be a convenient technology for the preparation of electrochemical biosensors which may allow commercialization of low cost devices on a large scale [128–130]. This technique allows the preparation of substrates in a variety of geometries at very low cost, especially when carbon inks are used [131]. Translation from conventional electrodes to screen printed designs has already succeeded in many cases, particularly for biosensors aimed at biomedical, environmental and industrial applications [130, 131].

The issue of sensor calibration in keeping the response within an accurate calibration domain is particularly significant in the development of chemo/bio-sensor networks [9]. In this regard, changes in the conditions of the transducing surface/layer cause changes in the response characteristics, necessitating the need for regular recalibration. The integration of electrochemical sensors in deployable WSN platform has to cope with the latter issue; this review will give particular emphasis to this aspect. Detection schemes combined with separation techniques such as microdialysis, electrophoresis, chromatography and laboratory-on-a-chip approaches [132] are not included here as these significantly increase the overall cost. Devices like electronic noses/tongues are also not covered because they are essentially an array of non-specific sensors. It is worthwhile to note that the response patterns obtained are not stable over time although their potential to extract complex information from the sensor array seems very powerful [133].

Anodic and cathodic stripping voltammetry [134–136] is commonly used as analytical method to detect ions with remarkable sensitivity, often in the ppb range or below, thanks to the "built-in" pre-concentration step, i.e., accumulation of analyte at the electrode [127]. Currently, anodic stripping analysis combined with screen printed electrodes seems to represent the best candidate for monitoring heavy-metals in remotely deployed submersible sensors. Work for the creation of in situ metals sensing platform has been pursued extensively in Buffle's and Wang's group [135, 137–140], and some commercial submersible voltammetric probes for trace element monitoring, e.g., Idronaut. The latter device has been used for in situ monitoring of heavy metals (Pb, Cd, Cu) at subnanomolar levels in coastal waters and results compared to established laboratory methodologies showing good accuracy over several days of monitoring [141]. However, calibration standards are stored within the device and the instrument is also quite bulky and prohibitively costly.

Stripping peak currents are not only proportional to deposition period and metal concentration but also depend on the area of electrode, diffusion coefficient of the species and convection rate [135]. Thus, environmental factors which may affect any of the latter properties would require a recalibration of the sensing device with obvious difficulty and cost to do this remotely in situ. While changes in the environmental temperature may be compensated by ex situ calibration at different temperature and use of a temperature probe, careful device design is required to avoid the other artefacts.

An additional agent can be required for some substrate types, e.g., Cu^{2+} inhibits the stripping response of Pb^{2+} whose concentration correlated with ICP-MS method only after masking with 0.1 M ferricyanide as complexing agent [142, 143]. This necessitates extra complexity in the remotely deployed sensing platform, such as that described in Sect. 3.3, where the masking agent would have to be stored and added to the sample within the instrument prior to analysis with the sensor. The use of reagents, where avoidable, is undesirable due to the complexity and associated increase in cost of the microfluidic system. The use of solid-phase extraction has been found to limit the use of reagents [144–148], suggesting a greater suitability for remote applications such as WSNs.

4.2 *Electrochemical Sensor Technologies Review*

4.2.1 Potentiometric Sensors

The principles of operation in potentiometric ISEs can be found elsewhere [149, 150]. Potentiometric sensors represent an interesting approach to environmental monitoring thanks to the simplification in the software/hardware interface to the sensor [123, 151, 152] and the very small power consumption requirement. The field of potentiometric sensors has gone through a revolution in the last 10 years with a major effort focused in the theoretical developments [153–161] which has led not only to a deeper understanding of these devices, but also more significantly to dramatic improvements in the detection limits, which has opened up new opportunities in environmental monitoring [162–164]. Solid-state ISEs are more convenient for remote monitoring than liquid-filled ISEs as they are compatible with microfabrication technologies and they are easier to miniaturize [150, 160, 165–167]. Conducting polymer-based solid-contact (SC) ISEs have produced significant results for the detection of Pb at concentrations comparable with current legislation requirements [168–170], i.e., down to 10 nM under laboratory conditions in simulated samples and down to ppb levels in real samples when standard addition methodology was employed [171, 172]. However, Radu et al. [173] showed that the calibration trends of these sensors are significantly distorted upon exposure with environmental samples which may indicate that sensors can be used only in combination with standard addition to compensate for the matrix effects.

Overall, these results confirmed that autonomous in situ environmental monitoring with potentiometric ISEs may be feasible for Pb, as the Water Framework Directive (WFD) has fixed its upper limit to 35 nM as standard for the environmental water quality. However, regarding a realistic employment of ISEs for remote monitoring, several aspects deserve further consideration. In potentiometry, the dependence of the signal response on the logarithm of the analyte activity has been considered as an inherent drawback [117] though it also means that sensors have a wider dynamic range. Potentiometric methods detect the activity and not the concentration of free ions, which can lead to ionic strength artefacts—this can also be an advantage as the activity is often the more relevant property in terms of bioavailability in many natural processes. One of the main hurdles for the use of ISEs in autonomous in situ applications is the complications of the conditioning protocols. Appropriate conditioning steps appear to be essential in order to achieve the very low detection limits reported in the literature, though guidelines for standardizing a protocol are not widely agreed upon [166]. Prolonged contact with a sample containing a strong interferent causes completely different reconditioning and subsequent distortion of the analytical response to the primary ion [117, 174]. Therefore, it may be necessary to make measurements over a short timescale, followed by longer storage periods in the conditioning media. The time required for the conditioning operations prior to measurement (e.g., conditioning step lasting several hours) may be a major drawback in terms of practicality of the sensing platform, limiting the capability of the sensor to operate at a high sampling rate. Using ISEs after long time periods of storage in a conditioning solution without calibration (all sensors are perfectly predictable) or limited to one-point calibration [175] (i.e., change in offset but not in sensitivity) would be very desirable, as the resulting device would be very simple and low cost signifying that they would be ideal for WSNs. In spite of extensive research in the area, it seems that obtaining SC-ISEs with reproducible standard potentials is still a substantial challenge [160] exhibiting very limited reproducibility of the measurements without frequent recalibration [176]. However, encouraging results on the sensor reproducibility and real samples analysis have been obtained by Saltisza et al. [172] using ISEs based on screen printed electrodes which may open the opportunity of calibrationless devices for in situ applications. Interestingly, Radu et al. [173] proposed the use of electrochemical impedance spectroscopy as means of self-diagnostics for remotely deployed chemical sensors in order to make a decision on whether a calibration is necessary or not, thus limiting the need of in situ calibration.

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4.2.2 Conductometric/Impedimetric Devices and Field-Effect Transistors

Conductometric devices measure the change in conductivity between electrodes or reference nodes due to the presence of a certain analyte [118, 123]. These sensors have been used in combination with enzymes, whose reaction with the analyte changes the sample conductivity [117, 120, 123]. In impedimetric sensors, changes in the resistive and capacitive properties of modified electrodes arising from the recognition event are measured by perturbation of the system using a small amplitude sinusoidal excitation signal [118]. Both the impedimetric and conductometric approaches do not require a reference electrode, which simplifies the experimental set-up and electronic circuitry [125, 152]. However, conductometric and impedimetric devices seem to have limited applicability in real samples due to their sensitivity to matrix effects such as changes in the ionic strength and the non-specific nature of these techniques [118, 119, 123, 127].

The field-effect transistor (FET) employs an electric field to control the conductivity of a channel between two electrodes, i.e., source and drain, embedded in a semiconducting material by varying the potential of a third electrode, the gate [118, 123, 177]. In biosensing applications, the metal layer at the gate is replaced by or coated with an appropriate biochemically sensitive surface, which is in contact with the analyte solution to produce the so-called ChemFET. ChemFETs, particularly ion-selective and enzyme FETs, have received considerable attention because they are suitable for weak signal and/or high impedance applications [118]. In addition, they seem strong candidates as disposable electronic biosensors particularly thanks to the low-power operation and the mass production capability [118, 125]. In particular, organic electrochemical junction transistors (OEJTs) have attracted certain interest for the construction of novel small, light weight, portable, disposable and low-cost sensor which seems suitable for mass production by using different way of printing [178]. However, a number of critical issues inhibit the feasibility of FET sensors for autonomous sensor networks. Firstly, establishing standard methods for the surface functionalization/patterning compatible with silicon-based device fabrication (e.g., enzyme immobilization and/or antifouling membranes) is a difficult and delicate task [118]. Secondly, the design of a miniaturized reference electrode compatible with the ChemFETs has yet to achieve the stability and performances comparable to the classical reference electrodes [179]. Thirdly, the detection sensitivity depends on solution ionic strength [180] and a desalting step would be an additional complication in an autonomous monitoring situation. Finally, the speed of the response, the recovery time, detection limit, and their cost as disposable platform compared to screen printing technology make them less attractive than they would appear to be conceptually [118, 123, 178].

4.2.3 Miniaturized Sensors

UltraMicroElectrodes (UMEs) have received substantial interest thanks to several favourable characteristics [181, 182]. For instance, decreasing the size of the electrode allows direct measurement in low ionic strength samples (e.g., freshwater) [127] and smaller capacitance currents are obtained, which increases the signal/noise ratio [181–183] improving the detection limit. It is significant to note that Bond and co-workers reported that measuring concentrations of redox species in the order of 10 nM using UMEs proved to be very challenging [182]. Decreasing the size of the electrode to the nanometer range seems impractical as imperfect seals cause stray capacitance to increase [181, 182]. In addition, as the current depends on the electrode size, its decrease has the obvious disadvantage of generating progressively smaller currents whose measurement, especially in the short time scales, may be challenging [182]. Miniaturized sensors offer the advantage of reducing the amount of material used per device (which can be significant particularly for certain biosensors) but they tend to be more susceptible to long-term stability problems, e.g., loss of biological molecules is progressively more serious as the electrode size decreases [123]. Overall, a trade-off in decreasing the size of the electrode exists.

Arrays of sensors enable new analytical approaches, e.g., multiplexed or redundant sensing, which are attractive features for cost-effective pollution control and protection of the natural environment [180, 183–185]. In a microelectrode array chip, simultaneous current measurements are possible using integrated circuits where the addressing hardware is built onto each electrode [186]. For instance, stripping analysis based on a gel integrated microelectrodes array have been employed for remote in situ monitoring and are the sensing core of Idronaut device [141, 183, 187]. On the other hand, potentiometric sensors array appear to have not advanced beyond the stage of laboratory research with no practical application in real samples being found [188].

The manufacturing of microelectrodes and microelectrodes arrays is still a complex process [189–191]. Among several methods of preparation, silicon-based microfabrication technology still offers probably the best results while microcontact printing could represent a cheaper method, although practical control of the geometric features and reproducibility is inferior [182, 184–186]. However, the long-term stability of microelectrodes and microelectrodes arrays is often questionable, e.g., defects in the metal layer, poor resistance to corrosion together with subsequent swelling and delamination of the metal layers [128]. Finally, multicalibration in an array becomes complicated and time consuming as the array response pattern becomes important and, as each electrode drifts, the pattern is unstable in use. In this regard, factorial regimes have been suggested to simplify these issues [192].

4.2.4 Enzyme Sensors

Enzymes constitute one of the most attractive approaches to transduction, as they facilitate amplification of the signal, due to the biological catalytic reaction, and display excellent selectivity, due to the high specificity towards a particular substrate [120, 123, 193]. As enzymes accelerate the equilibrium formation of a chemical reaction, sensors based on enzymes are intrinsically reversible and may be regenerated [123, 193], which is beneficial for lowering the cost basis. Screen printing and inkjet formulations for the preparation of disposable enzyme-based sensors have been explored [131]. The principal type of detection for these sensors is amperometric and while potentiometric [174] and conductometric [193] approaches have also been used, these tend to be more dependent on the ionic strength and pH of the sample solution [123], i.e., less suitable for autonomous remote monitoring. However, in sensors wherein the products of enzymatic reaction are gaseous, conductometric detection can be very successful when coupled with a gas-permeable membrane to remove most interferences [123].

It is important to note that it is preferable for a sensor to detect a specific analyte rather than the total amount of similar compounds. This is the case of enzyme sensors which respond to a class of compounds, e.g., phenols, organophosphate, carbamates, etc., more than to one specific compound [3, 194–196]. For instance, detection of common pesticides is based on the inhibitory effect that these chemicals have on acetyl-cholinesterase (AChE) [131, 197]. Yet, this type of sensors may be interesting as early-stage alarms. Thus, for instance, enzyme disposable biosensors proved useful for assaying a phenol "index" in wastewater, surface and river water with shelf stability up to months and detection limits down to nanomolar levels, although sensors responses differ in absolute magnitude and requires in situ calibration [3]. Entrapment of enzymes in gel formulations and/or water-based carbon ink, compatible with screen printing and capable of improving the enzymatic stability, yet holds great promise for the preparation of enzyme biosensors [123, 130, 193]. General concerns for enzyme sensors are connected to the shelf-stability and cost of the biomaterial, co-substrate concentration changes in time and space, biofouling, redox interferents, reproducibility over time and operational lifetime of the device [118, 123, 131, 198–202]. Despite the success of glucose sensors [3, 120, 193], the above reasons probably explain the lack of commercial enzyme-based analyzers applied to in situ environmental monitoring of specific targets.

Whole-cell sensors have been reported for environmental monitoring in replacement of enzyme sensors because they obviate the need for enzyme purification and they may extend the lifetime of the device [203]. Overall, these sensors are probably more suitable for the evaluation of toxicity and an early stage alarm than sensing a particular analyte [116]. Nevertheless, it is important to note that Unisense offer a sensor based on a biofilm for NO_3^- and NO_2^- monitoring with a month lifetime which is claimed to be suitable for in situ applications. The sensor has size comparable to a normal pH-meter but, with a cost of approximately €800, its integration in deployable modules is quite costly and its operational continuous monitoring is said to be limited by the charge of the battery, i.e., up to 100 h without need of repeated calibrations.

4.2.5 Affinity Sensors: DNA and Immunosensors

In environmental monitoring, DNA sensors have been applied to the detection of nucleic acids, e.g., *Escherichia coli*, environmental pollutants and carcinogenic compounds [116, 117, 121] while immunosensors have been mainly employed in order to monitor pesticides, herbicides and virus toxins [122, 124]. The specificity of the sensors is defined by the stability constant, which for antibody-antigen binding is in the order of 10^8–10^{10} LM^{-1}, i.e., three orders of magnitude higher than enzyme-substrate binding [122]. Difficulties in patterning of the biomaterials on electrode substrates, i.e., functional orientation, cost, lifetime and reproducibility of the biomaterial layers, even without considering the eventual labelling, are the main drawbacks for these sensors [118, 121, 122]. In addition, poor reproducibility and low specificity of the sensors during operation have led to unsatisfactory results in terms of further commercialization for trace analysis, e.g., environmental pollutants [122, 124], and remote sensing platforms. Molecular imprinting may offer a cheap and valuable alternative as recognition element with longer shelf and operational lifetime [204]; however, their poor performances, especially in terms of selectivity, are still a main limiting factor [205].

4.3 Conclusions

Anodic stripping voltammetry in combination with screen printed electrodes (perhaps also modified for solid-phase extraction), which may be regenerated and reused without re-calibration, seems to be the best candidate for autonomous in situ sensing of heavy metals thanks to very low detection limits achieved, fast response time and relative low cost. It is significant that ISEs may allow monitoring of Pb below the current legislation concentration limits as this detection mode would further decrease the device's power consumption. Regarding other toxic chemicals targeted by WFD legislation, such as herbicides, it appears that research is still focused on the fundamental studies and we are still far from a practical device which can claim to detect a particular analyte excluding an eventual interferent bias. Therefore, a priori knowledge of the interferents is required or the sensor should be combined with separation techniques to avoid a large number of false detections which, unfortunately, hampers the advent of deployed sensing platform because of the increased costs.

It is significant to note that coulometry as a detection mode has not been extensively applied to commercial devices although it may represent a viable alternative for fast analysis when coupled to a microfluidic device able to accurately control small sampling volumes i.e., μL and below. Indeed, the coulometric analysis is independent from the kinetics parameters and the physical properties of the system, e.g., enzyme activity, electrolyte concentration, temperature, viscosity, etc. which would render the device less prone to sample matrix changes and may not require calibration. For instance, the Abbott FreeStyle™ glucose tester produced at the rate of 10^9 devices/year is actually based on thin layer micro-coulometer with a submicroliter fluidic sampling.

At the present state, the preparation of disposable sensors seems the simplest solution in order to cope with needs and issues arising from a deployed platform but new approaches are still required to increase ruggedness, shelf- and operational lifetime of the sensors. This conclusion emphasizes the fundamental research in nanotechnology as the key strategy to design, engineer and control the sensing layer at the electrode interface thus addressing these needs.

5 Instrumentation and Data Processing

5.1 Introduction

Although elements within the chemical sensor research community (such as gas, water and electrochemical sensing) are excelling within their own fields, a key question that often goes unanswered is how to make practical implementation of such newfound sensing capabilities. The literature, in these cases, is rich with past and current studies with demonstrations of highly selective and sensitive chemical measurements [206]. Correspondingly, studies within the technological domain describe how sensing platforms can easily incorporate chemical sensors [102, 103]. However, there are relatively few reports describing the application of chemical sensing capabilities outside the confines of the laboratory environment and even less so describing chemical sensor integration into autonomous WSNs for in situ deployments [5]; examples of these will be outlined within this section. Furthermore, it has been widely recognized that many chemical parameters of interest vary broadly in the temporal and spatial domains and that the current manual-based sampling methods employed by government agencies is inadequate for understanding the underlying principles of these changes within the environment [207–209]. Therefore, there is a need for the creation and deployment of chemical sensing systems capable of performing complex analytical measurements in situ i.e., to join these two independent domains [8]: the molecular and digital worlds. It has been generally recognized [210] that a practical environmental chemical sensing system must:

- Be fully autonomous
- Operate for long periods of time
- Sample at periods when "events" occur
- Reflect needs in terms of spatial and/or selective measurements
- Successfully communicate the sensor data remotely
- Present the data to relevant users in an easy to use and understandable manner

In order to fully realize such a system, a multidisciplinary approach must be undertaken involving teams of chemists, electronic/mechanical/telecommunications engineers, computer scientists, middleware managers, visualization experts, web designers, etc. all working together towards a common goal. It is clear that this effort is not trivial and it is not surprising that few entities can achieve such an objective. The difficulties lie mainly in the nature of chemical sensors where they frequently encounter problems in their response characteristics such as baseline drift and changes in sensitivity (usually reduction effects) [9]. In fact, this goal has been identified in a recent Analytical Chemistry Editorial as the next "grand challenge" for analytical chemists [211]. However, there are those who have been fortunate with resources to include cross-disciplinary expertise, amongst others, and therefore have risen to the challenge of implementing WSNs.

Clearly, distributed real-time chemical sensing is vital for air- and water-based areas at risk; however, the costs associated with current deployments place limitations on the spatial density and/or selectivity of these sensors for future demands. It is therefore important to drive down the cost of the sensing platforms and invest in energy scavenging capabilities [212], where possible, to maximize the sensing lifetime and minimize the persistent maintenance costs and initial cost base. To achieve this, every element within the architecture of such an end-to-end sensing system must be examined. A common approach adopted by those in this area has been largely based on standard WSN set-ups [6, 213] where nodes equipped with chemical sensing capabilities communicate through central gateways/coordinator nodes to remote storage centres and eventually to end users. Figure 9 depicts this approach showing the progression of information from a single node to the system's

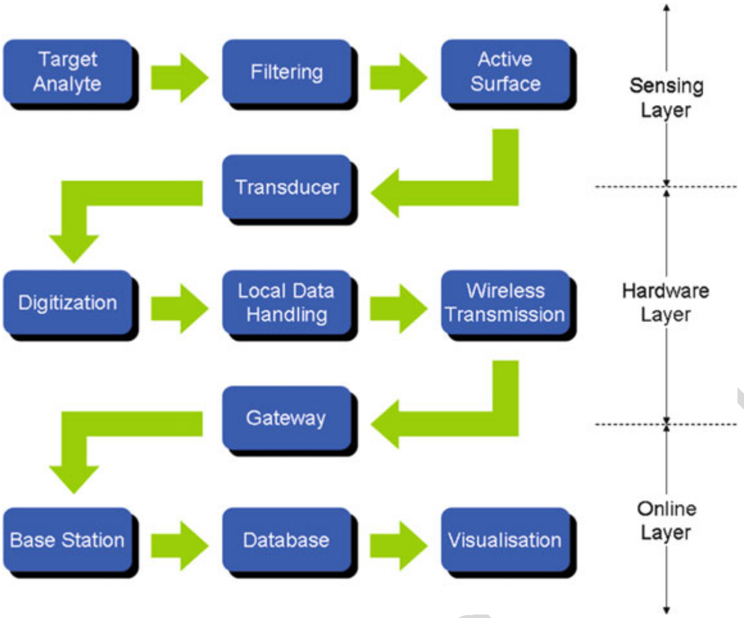

Fig. 9 Flow diagram tracing the sensory information path from the target analyte to the end user via a single sensing node-single, single base station model

end device. Here the information is traversed along three distinct stages or "layers." Firstly, the *sensing layer* is denoted as that where chemical interactions occur; a target analyte is identified for measurement, followed by filtering and/or anti-biofouling sub-systems and finally allowing the analyte to interact with the active surface. The active surface will change in some measurable properties, e.g., resistance, optical, potential, etc. and thus opening a doorway into the *hardware layer* via the transducer. Specifically, the transducer conditions the resulting signal into a measureable form for a microcontroller/microprocessor to digitize. The controller's responsibilities range from sampling frequency, sub-system actuation, timing, data storage and communications to a base station located in the *online layer* via gateway platforms. The *online layer* in this context is where a human user interacts with the sensed data. The data is received by the base station and stored on a database located on a server or on the "cloud" where data is always accessible via the Internet. Finally, users can interact with the sensor network(s) through media such as Internet browsers, smart phones/tablets, etc. Depending on the complexity of the architecture, the users can propagate back through the sensing chain and alter properties such as sampling frequency, nodal communication assignment, diagnostics, etc. Additionally, the basic node-base station configuration can have multiple network topologies with scale-up to include the most commonly employed type (i.e., star configuration) and more complex systems (e.g., tree and mesh set-ups); all of which are considered classical and reported in review articles [214].

The ability to harvest chemical information from target locations and sustain this ability over long periods of time can open up a new world of information from target sensing areas. The reasons for pursuing such a task lie in the potential to recognize patterns in the data and predict "events" based on historical and/or other sources of information e.g., weather data. Moreover, opportunities now exist to unveil new sources of information describing a system which were otherwise unavailable and can ultimately allow for a further understanding of the dynamics of a target area. In other words, such a sensing approach essentially results in a time series of environmental data embedded with specific "signatures" that need to be classified so that it can ultimately be used for the prediction of events. Analysis of this data is an important aspect of environmental monitoring [215] and a generic approach can be employed for many target analytes.

5.2 Data Processing Case Study

This approach can be illustrated by analyzing harvested data from the air monitoring domain that was introduced in Sect. 2. With clearly defined limits on emissions being released into our environment, there are national and international agencies in place to regulate and monitor such emissions. Considering data gathered from a single borehole well on a landfill site over a 4- to 5-month period, acquired using the gas sensing platform described in Sect. 2.3, a comparison can be made between the manual-based sensing method and the autonomous sensing device placed in situ. To recap, two of the prominent emission gases from landfills (i.e., CO_2 and CH_4) have strict limits in place (i.e., 1.5% and 1%, respectively). Figure 10 shows a plot of CO_2 emissions with vertical lines simulating a sampling routine performed by site personnel or governing inspectors every workday, i.e., Monday at 11:00 a.m. in this case. From the plot it can be seen that a number of "events" occur between each manual sampling routine (labels A–E), i.e., where the concentration of CO_2 rises and is missed by adopting the manual sampling method. Similarly, Fig. 11 shows the CH_4 gas constituent for the same data acquisition duration.

To further quantify the discrepancy between periodic measurements and continuous in situ monitoring, as visually demonstrated by points A–E in Figs. 10 and 11, AU4 the 4-month dataset has been subjected for a more rigorous temporal analysis. To this end, the validity of data points at regular periods (i.e., weekly or monthly to simulate the manual sampling routine) was assessed with respect to the whole dataset duration by means of two statistically descriptive components: the "maxima percentage error" defining the difference between the maximum of the periodic data points and the maximum in situ measurement; and the "averages percentage error" describing the difference between the average of the periodic data points and the average in situ measurement. Such information is beneficial as the selection of the day of week or of month can have a substantial impact of achieving a representative time profile of a target sensing area and each gas constituent measured.

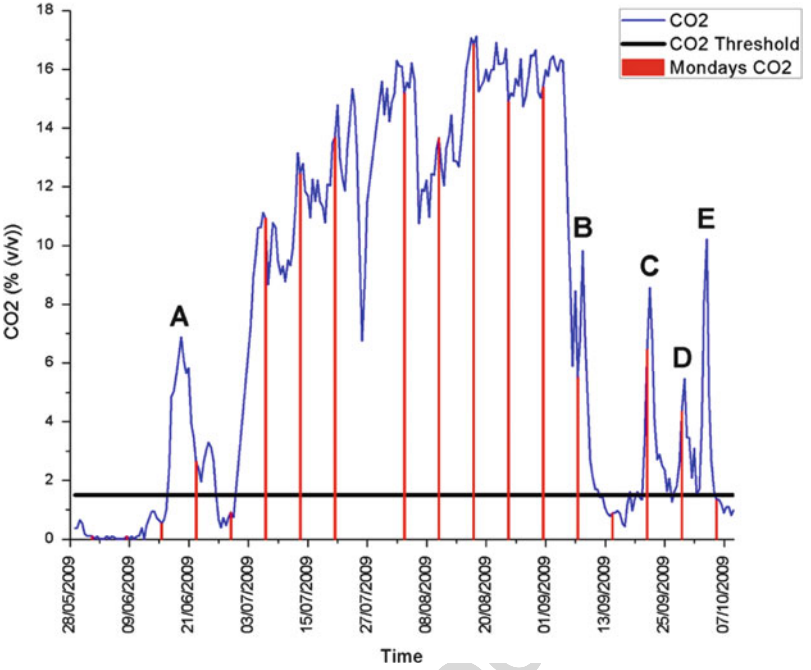

Fig. 10 Harvested CO_2 emission data from 4-month deployment on an active landfill site (*blue line*: measured emissions; *black line*: legal gas limit; *red lines*: simulated manual weekly sampling; *A–E*: concentration spikes unaccounted for by a weekly measurements)

To illustrate this, the percentage errors of these two statistics were compiled for weekly sampling in Table 1. It can be seen that by taking a sample on Fridays, the maxima error was 0% for CH_4; however, the averages error was as high as 13.7%. In terms of averages error, it appears that Wednesdays were best for CO_2 while Mondays were best for CH_4. In other words, while optimizing the time to sense one target analyte, one cannot necessarily conclude that this is representative for every target thus presenting a challenge in choosing an optimum day for sampling. It should be mentioned at this point that weekly measurements is a relatively high sampling frequency for this process. It has been discussed previously that only monthly measurements are required for compliance with existing landfill regulations. To this end, the same comparison can be drawn by interpolating monthly measurements from the full dataset. Table 2 shows the same data when manual measurements are recorded on the first Monday, Tuesday. . . Friday of each month. As a result, the percentage error has increased dramatically for both statistically compiled parameters for this location when compared to weekly measurements shown in Table 1. It is clear that the granularity of data from monthly to weekly has shown an overall greater accuracy towards a representative time profile of this site. Furthermore, neither monthly nor weekly measurements appear

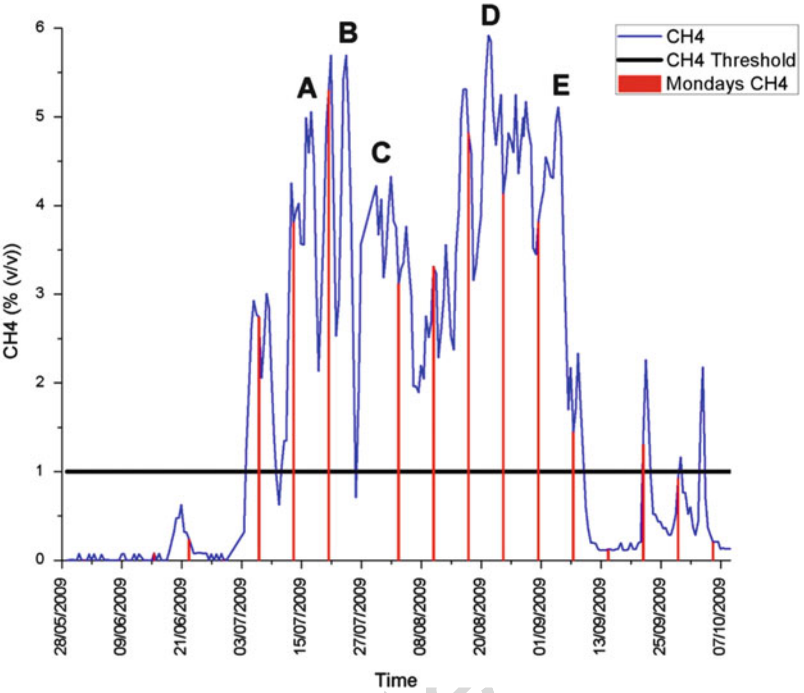

Fig. 11 Harvested CH_4 emission data from 4-month deployment on an active landfill site (*blue line*: measured emissions; *black line*: legal gas limit; *red lines*: simulated manual weekly sampling; *A–E*: concentration spikes unaccounted for by a weekly measurements)

Table 1 Maximum and average percentage errors for weekly workday readings interpolated from the full dataset

	CO_2		CH_4	
Weekly	% Max. error	% Avg. error	% Max. error	% Avg. error
Mondays	1.59	3.06	3.63	0.20
Tuesdays	8.02	0.70	6.43	0.97
Wednesdays	3.92	0.00	7.70	5.05
Thursdays	6.94	1.24	2.80	5.31
Fridays	4.96	15.20	0.00	13.69

to be sufficient for understanding the dynamics occurring at this site, hence affirming the value of sensors placed in situ.

Another important factor in environmental monitoring when considering temporal sampling is the number of breaches that are missed when sampling as infrequently as once per month or once per week relative to the capabilities of a dedicated chemical sensing platform. A simple data processing tool to evaluate this is a threshold algorithm which easily compliments environmental data as there are strict quantitative limits in place by governing authorities. Table 3 shows two datasets, the first is how many breaches are missed when sampling on a weekly (workday) basis, the

Table 2 Maximum and average percentage errors for monthly readings (first Monday, Tuesday.... Friday) interpolated from the full dataset

	CO_2		CH_4	
Monthly	% Max. error	% Avg. error	% Max. error	% Avg. error
First Mondays	11.29	15.06	16.34	23.35
First Tuesdays	8.02	7.98	10.28	4.27
First Wednesdays	3.92	12.43	8.49	10.99
First Thursdays	6.94	4.17	9.38	17.93
First Fridays	4.96	0.76	4.75	20.94

Table 3 Percentage of breaches missed, relative to the full dataset, when sampling on a (a) weekly and (b) monthly basis

(a)

Weekly	CO_2 breaches missed (%)	CH_4 breaches missed (%)
Monday	68.25	48.81
Tuesday	68.25	48.81
Wednesday	68.25	49.60
Thursday	67.86	49.21
Friday	66.67	49.21

(b)

Monthly	CO_2 breaches missed (%)	CH_4 breaches missed (%)
First Mondays	71.83	51.59
First Tuesdays	71.83	51.59
First Wednesdays	71.83	51.59
First Thursdays	71.43	51.59
First Fridays	71.43	51.98

second is how many are missed when sampling on the first day (Monday, Tuesday..... Friday) of each month; both compilations are relative to the full dataset.

Although the difference can be expected to be high when comparing twice-per-day sampling to weekly sampling, the averages of 68% (CO_2) and 49% (CH_4) of breaches missed are excessively large numbers when ideally there should be no breaches at all. This grows to 72% (CO_2) and 52% (CH_4) when sampling less frequently at once per month. The important aspect to derive from this is that by employing a manual sampling regime, a high percentage of legal limit breaches can easily be missed which can result in disastrous consequences.

6 Conclusions and Future Perspectives

In this contribution we have tried to give some flavour of the exciting possibilities that will arise as the cost of chemo/bio-sensing platforms capable of functioning autonomously for months, if not years, is driven down, enabling larger-scale deployments to happen. The success of operation of these platforms in collecting and visualizing an abundant wealth of insightful data on gas and water characteristics, as exemplified by our collaborations with governmental and industrial partners, demonstrates the usefulness of such platforms in any environmental monitoring application. This work represents the realization of autonomous sensor networks for environmental monitoring by developing sophisticated platform technologies that form the basic building blocks of WSNs. The systems described in Sects. 2.3 and 3.3 for air and water monitoring, respectively, have proven their performance in terms of accurate consistency and reliability; the focus henceforth will be the progression towards lower-cost and less power intensive systems such that a denser distribution of sensor platforms can be attained. Information of incredible value to individuals and society will become accessible for the first time, providing a basis for better understanding of the processes that affect our environment, and therefore enabling effective strategies for enhancing the quality of the environment to be implemented. Clearly, ultra-low-cost, reliable, and durable chemo/bio-sensing devices are the key to future massively scaled deployments of such WSNs. Electrochemical sensors, as discussed in Sect. 4, show promise with low cost and accuracy being readily achieved though continued development is necessary to a longer-term consistency in sensing accuracy. Considering the big picture, moving from the current state of the art to the futuristic vision will require fundamental breakthroughs in materials science in order to dramatically reduce the cost of implementing the lab-on-chip liquid handling technologies that underpins the water quality analyzers described previously [216]. In contrast, future platforms are likely to incorporate biomimetic polymer actuators more reminiscent of artificial muscles rather than conventional pumps and valves [217, 218]. This will demand a close alignment of fundamental science and applied engineering research effort—institutions that implement this on the ground through closely integrated teams of researchers will be the places where these advances will happen.

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