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Novel biospectroscopy sensor technologies towards environmental health monitoring in urban environments

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A B S T R A C T

Biospectroscopy is an emerging inter-disciplinary field that exploits the application of sensor technologies [*e.g.*, Fourier-transform infrared spectroscopy, Raman spectroscopy] to lend novel insights into biological questions. Methods involved are relatively non-destructive so samples can subsequently be analysed by more conventional approaches, facilitating deeper mechanistic insights. Fingerprint spectra are derived and these consist of wavenumber–absorbance intensities; within a typical biological experiment, a complex dataset is quickly generated. Biological samples range from biofluids to cytology to tissues derived from human or sentinel sources, and analyses can be carried out *ex vivo* or *in situ* in living tissue. A reference range of a designated normal state can be derived; anything outside this is potentially atypical and discriminating chemical entities identified. Computational approaches allow one to minimize within-category confounding factors. Because of ease of sample preparation, low-cost and high-throughput capability, biospectroscopy approaches herald a new greener means of environmental health monitoring in urban environments.

1. Introduction

Urbanization is a complex phenomenon giving rise to a large array of changes in environmental and lifestyle factors (Zhu et al., 2011). Urban environmental pollution is greatly increased by human and industrial activities; as a consequence, such settings are often used as a focal point for contamination studies (Callender and Rice, 1999). Emissions from industrial/municipal activities as well as the use of motor vehicles increase the need for biomonitoring of environmental contaminants, particularly within urban settings. Environmental contamination and pollution may occur on land, in water or in air. According to Satterthwaite (1993), Waller (1991) identified urban air contaminants to include smoke/suspended particulates, sulphur dioxide, sulphuric acid, polycyclic aromatic hydrocarbons (PAHs), nitric oxide, carbon monoxide and some heavy metals. Most of these listed contaminants are found to be present in soil (Morillo et al., 2007) and water with increased contaminant concentrations in industrial areas (Li et al., 2001; Zhang et al., 2005). The effects of exposure to listed contaminants on health possibly arise from their ability to be readily absorbed following inhalation or ingestion and distributed within the systemic circulation. This underlies the need for indicators (or biomarkers), which correlate the presence of these contaminants within the environment and possible health outcomes; insight into mechanism(s) of action are also critical. In addition, another major consideration within urban environmental settings is the pathophysiology of viral or bacterial infection mechanisms; novel sensors could track pathogens or readily identify infected tissues or organisms. This review examines the possible role of biospectroscopy techniques and approaches as a novel sensor-based technology for application in a wide range of contexts that could relate to environmental health monitoring in urban environments. There is an urgent need for low-cost, high-throughput, and contamination-free biosensor technologies.

1.1. Biomarkers of health status in urban environments

Environmental contaminants are thought to induce certain structural and conformational alterations in biomolecules (*e.g.*, DNA, protein), exerting their toxic potential *via* diverse mechanisms including endocrine disruption, genotoxicity, epigenetic alterations and immunosuppression (Smits et al., 2002; Østby et al., 2005; Grandjean and Landrigan, 2006; Tian et al., 2012). Hence, such alterations can be exploited as indicators which provide information regarding the presence of or exposure to an environmental contaminant (Vinzents et al., 2005; Malins et al., 2006). Biological

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markers (biomarkers) are indicators of variation in cellular or biochemical components, processes, structure or functions measurable in biological systems and/or samples. They generally could be classified either as biomarkers of exposure, effects or susceptibility (Bearer, 1998). The use of biomarkers in biomonitoring often permits the non-destructive sampling of tissues or bodily fluid (*e.g.*, urine, blood) with the aim of providing accurate estimates of internal or effective dose and organ function. Moreover, the level of understanding as regards the biology of the target species (*i.e.*, humans) improves the likelihood that the biomarker responses will be interpreted correctly (Forbes et al., 2006). Biomarkers developed in human and environmental toxicology have proved to be useful as biological, physiological or histological indicators of either exposure to specific chemicals or as early warning indicators of specific diseases/syndromes (Fairbrother et al., 1989; McCarthy and Shugart, 1990; Timbrell, 1998). Biomonitoring of environmental contaminants using biomarkers has allowed quantitative determination and assessment of environmental pollution ranging from exposure to heavy metals and chemicals to the effects of pesticides by monitoring such agents, their metabolic products and/or conjugates with biomolecules in either serum, urine or other body fluids and tissue samples (Ruchirawat et al., 2002; Budnik and Baur, 2009; Kasperczyk et al., 2012).

1.1.1. Recruiting sentinel organisms to monitor environmental health

Certain organisms serve as bioindicators of environmental health and are often used in biomonitoring studies (Table 1). These organisms are able to accumulate environmental contaminants and may be used to monitor the presence and toxic effects of a given agent over time, allowing in certain cases a comparison between contaminant levels in geographically different areas. Effects of contaminants on marine organisms at molecular, cellular, tissue/organ and organism level is predominantly carried out using molluscs (mainly mussels, *Mytilus* sp.) (Cajaraville et al., 2000; Nasci et al., 2002) or fish (Schwaiger et al., 1997; Koehler, 2004) as bioindicators. Lichens are another group of organisms proposed as bioindicators of air quality due to their sensitivity to environmental changes, which could alter their constituents and/or specific parameters of wellbeing (Gries, 1996; Blasco et al., 2006). The concentration of chlorophyll $a+b$ in lichens is reportedly altered by vehicle traffic numbers (Carreras et al., 1998) and by urban emissions (Zambrano and Nash, 2000), with the quality of species distribution improving with increasing distance from urban areas (Larsen et al., 2007). Other sentinel organisms include earthworms (Kennette et al., 2002; Dai et al., 2004; Martin et al., 2005) and the land snail (Regoli et al., 2006).

Table 1
Biomarkers in sentinel organisms.

Organism	Biomarkers
Molluscs	Lysosome membrane stability, Lysosomal lipofuscin, Lysosomal neutral lipid, CaATPase activity, Catalase activity, Total oxidant scavenging capacity, Acetylcholinesterase activity, Malondialdehyde, DNA damage/micronucleus formation, Glutathione-*S*-transferase in haemolymph, [a]Metallothioneins
Fish	Lysosome membrane stability, Lysosomal lipofuscin, Glutathione-*S*-transferase, Glutathione peroxidase, Glutathione reductase, DNA damage/micronuclei, Gonad morphology/atrophy, CYP1A [Ethoxyresorufin-*O*-deethylase (EROD)], Vitellogenin steroid hormones, Acetylcholinesterase activity, [a]Metallothioneins
Lichens	Photosynthesis, Chlorophyll content/degradation, Endogenous auxin levels, Ethylene production

[a] Biomarkers of exposure to specific classes of chemicals particularly heavy metals such as lead, cadmium, etc. (Source: Conti and Cecchetti, 2001; Viarengo et al., 2007).

1.2. Biosensing technologies

The identification of biochemical pathways through which disease processes may occur within organisms is possible using technologies which enable the evaluation of particular chemical “fingerprints” (metabolite profiles or gene/protein alterations) that specific cellular processes leave behind (Mollerup et al., 1999; Kenny et al., 2005; Welthagen et al., 2005). These signatures of effect(s) serve as cellular biomarkers detected and measured in biological cells and tissue samples, and may indicate exposure to certain factors capable of initiating or altering cellular processes. Analytical techniques (chromatography, microscopy and spectroscopy/spectrometry) are employed to detect biomarkers within cells or tissue samples (Zhang et al., 2004; Bi et al., 2007), which mostly serve as indications of biochemical toxicity, initiation and progression of disease conditions or the presence of certain chemicals within given samples. Biosensing techniques undergo constant protocol modifications to increase precision, minimize/eliminate bias, achieve certain sensitivity/specificity/selectivity levels and expand detection/concentration limits. Recent techniques have explored the potential application of nanoparticle technology to enhance optical imaging and improve sensing technologies (Qian et al., 2007; Welsher et al., 2011). However, this review focuses on the application of spectrochemical methods in understanding the various changes within biological samples arising from interaction(s) with environmental contaminants. It seeks to explore the potential of such methods as a sensing technique for environmental health biomonitoring, particularly within the urban environment.

2. Biospectroscopy

The interrogation of biological specimens using spectrochemical methods of analysis with the aim of acquiring information pertaining to a cellular entity based on its inherent ability to absorb, reflect, bend or scatter radiation as a consequence of its chemical bond structure could be defined as biospectroscopy. Regarding biological samples, absorption or emission of radiation is related to discrete vibrational and rotational transitions within a molecule representing therefore, the different chemical bonds present (German et al., 2006). Vibrational spectroscopic techniques have become potential tools for non-invasive optical tissue diagnosis (Kelly et al., 2011a). Applications of spectroscopic techniques in biological studies have particularly increased in clinical investigations relating to cancer screening in human tissue, perhaps due to their ability to differentiate between normal and diseased tissues (Horsnell et al., 2010; Gajjar et al., 2013) and cell types (German et al., 2006).

The analytical value of spectroscopy [*e.g.*, infrared (IR) spectroscopy] is based on the fact that spectral bands occurring at more or less localized positions in the spectrum can be correlated to the presence/absence of characteristic structural features in the interrogated sample (Stuart, 2004). Cells or tissue samples of organisms exposed to a complex mixture of substances which constitute pollution within the urban environment could be interrogated using spectrochemical technologies combined with suitable computational data processing tools allowing the detection and measurement of biomarkers present within the sample following toxic insult (Barber et al., 2006; Llabjani et al., 2011; Pang et al., 2012). Understanding that constituents of biological cells absorb in the mid-IR region ($\lambda = 2$–$20\ \mu m$) based on the chemical bonds present, with specific absorption regions and spectral bands attributed to lipids ($\approx 1750\ cm^{-1}$), carbohydrate ($\approx 1155\ cm^{-1}$), secondary structure of proteins (Amide I, $\approx 1650\ cm^{-1}$; Amide II, $\approx 1550\ cm^{-1}$) and DNA/RNA ($\approx 1225\ cm^{-1}$; $\approx 1080\ cm^{-1}$) (Kelly et al., 2011b), allows the

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