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Rapid screening and identification of chemical hazards in surface and drinking water using high resolution mass spectrometry and a case-control filter

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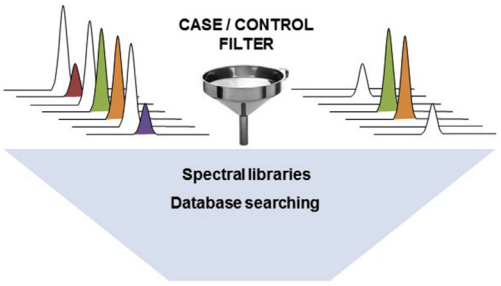
HIGHLIGHTS

- Non-target suspect screening of polar contaminants in water matrices.
- 'Case-control' data processing to efficiently reduce HRMS data complexity.
- Rapid, <24 h response time to chemical hazard screening in real-life case studies.
- >90% of target compounds (n = 46) positively screened in samples at 1 μg/L.

GRAPHICAL ABSTRACT



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ABSTRACT

Access to clean, safe drinking water poses a serious challenge to regulators, and requires analytical strategies capable of rapid screening and identification of potentially hazardous chemicals, specifically in situations when threats to water quality or security require rapid investigations and potential response. This study describes a fast and efficient chemical hazard screening strategy for characterising trace levels of polar organic contaminants in water matrices, based on liquid chromatography high resolution mass spectrometry with post-acquisition 'case-control' data processing. This method allowed for a rapid response time of less than 24 h for the screening of target, suspect and non-target unknown chemicals via direct injection analysis, and a second, more sensitive analysis option requiring sample pre-concentration. The method was validated by fortifying samples with a range of pesticides, pharmaceuticals and personal care products (n = 46); with >90% of target compounds positively screened in samples at 1 ng mL^{-1}, and 46% at 0.1 ng mL^{-1} when analysed via direct injection. To simulate a contamination event samples were fortified with compounds not present in the commercial library (designated 'non-target compounds'; fipronil and fenitrothion), tentatively identified at 0.2 and 1 ng mL^{-1}, respectively; and a compound not included in any known commercial library or public database (designated 'unknown' compounds; $8Cl^-$ perfluorooctanesulfonic acid), at 0.8 ng mL^{-1}. The method was applied to two 'real-case' scenarios: (1) the assessment of drinking water safety during a high-profile event in Brisbane, Australia; and (2) to screen treated, re-circulated drinking water and pre-treated (raw) water. The validated workflow was effective for rapid prioritisation and screening of

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suspect and non-target potential hazards at trace levels, and could be applied to a wide range of matrices and investigations where comparison of organic contaminants between an affected and control site and or timeframe is warranted.

1. Introduction

The World Health Organization attributed an estimated 4.9 million deaths to management of, and exposure to, known chemicals in 2004 (Prüss-Ustün et al., 2011). Due to the large number of new chemicals registered every year, and the relatively small proportion of which are thoroughly tested, the potential risk to biota and human health is largely unknown (Muir and Howard, 2006). Sources of hazardous chemicals include chemical manufacturers, service stations, hazardous materials waste sites, and common household products Environment (European Environment Agency, 2011). The relatively uncharacterised nature of hazardous chemicals poses a serious challenge for regulators in charge of safeguarding human health and environmental wellbeing.

Historically, analytical methods used for aquatic monitoring typically cover only a small fraction of known, target chemicals. This approach is limited in situations where an issue of concern is identified, such as deliberate or accidental chemical spills, or extreme weather events (e.g. floods, heavy rain or droughts that can generate contaminant concentration pulses of ecotoxicological relevance to the aquatic environment) but the link to a specific chemical hazard is unclear (Escher et al., 2013). Recently advances in high resolution mass spectrometry (HRMS) and data processing software has seen a rise in non-target analytical strategies (Herrera-Lopez et al., 2014; Gomez et al., 2010, 2012; Gómez et al., 2011; Krauss et al., 2010; Ibáñez et al., 2008; Bletsou et al., 2015; Schymanski et al., 2015; Baz-Lomba et al., 2016), and particularly suspect screening (Gago-Ferrero et al., 2015; Pochodyloa and Helbling, 2017; Badea et al., 2015), to address the need for analysis of an increasing number of analytes in complex mixtures. 'Non-target analysis' refers to detection and tentative identification of analytes for which chemical reference standards are unavailable. 'Suspect screening' is a form of non-target analysis whereby analytes are identified on the basis of accurate mass, elemental composition and structure prediction, followed by database or library searching. 'Unknown' non-target analysis is an unbiased approach, and is usually performed after targeted and suspect screening. It involves different data filtering strategies to reduce the size of the search space, followed by assignment of probable chemical formula based on MS/MS fragmentation and other strategies (Andra et al., 2017). Non-target analyses have been used to investigate contaminants in waste (Gomez et al., 2010; Gago-Ferrero et al., 2015) and surface waters (Ibáñez et al., 2008; Bletsou et al., 2015; Badea et al., 2015; Gomez et al., 2008; Ruff et al., 2015), foodstuffs (Gomez-Ramos et al., 2013, 2016; He et al., 2016), and forensic applications (Bletsou et al., 2015; Fels et al., 2016; Montesano et al., 2016), but have not yet been applied in response to time-critical environmental hazard assessment.

There is a need for analytical strategies capable of rapid non-target and suspect screening for identification of hazardous chemicals, specifically in situations where exposure is unknown or involves complex chemical mixtures, and requires an immediate response. Data reduction strategies based on comparison of 'case' samples (which have an outcome of interest or concern), and 'control' samples (which do not have the observed outcome/concern) can be used to rapidly analyse the large amount of data generated during screening experiments using HRMS. The case-control approach has been successfully used in proteomics and metabolomics studies (Zhang et al., 2014; Mapstone et al., 2014), but currently has limited use in environmental monitoring applications, including water quality testing. Briefly, a peak-finding algorithm is used to identify molecular features across different samples, followed by case-control comparison to identify suspect features for subsequent identification by searching against available spectral libraries, and to eliminate any matrix-specific interferences. The combination of accurate mass data and statistical evaluation of sample constituents allow for the rapid extraction and prioritisation of the most important chemical suspects for further identification.

Here we present a new approach for the rapid identification of unknown polar chemical hazards in water, based on the post-acquisition comparison of samples in a case–control setting. High resolution quadrupole time-of-flight tandem mass spectrometry (QTOF-MS/MS) is used together with "smart" data-mining software to (1) develop a rapid case-control screening method to identify the presence of potential hazardous chemicals; (2) validate the method using fortified water samples and simulate a contamination event; and (3) apply the screening strategy to raw and drinking water samples in two independent 'real-case' scenarios.

2. Experimental methods

2.1. Chemicals and standards

A standard working solution of 46 model compounds was prepared in methanol at 1 mg/L concentration (Table S1). A surrogate standard containing 12 labelled compounds at 1 mg/L was added prior to sample extraction, and used to monitor method performance; an injection standard of acetylsulfamethoxazole-d4 at 10 ng/mL was added prior to injection and used to monitor instrument performance. Calibration standard solutions were prepared in 20% methanol. All reagents and standards were high purity analytical grade (refer to Supplementary Material).

2.2. Sample preparation

Model chemicals were fortified in 1 L drinking water. Target chemicals (Table S1) were fortified at concentrations of 10, 5, 1, 0.5 and 0.1 ng mL^{-1}. Non-target chemicals (Table 1) were fortified in samples at levels of 10, 1 and 0.2 ng mL^{-1}, with the exception of 8 Cl^- PFOS, which was fortified at 40, 4 and 0.8 ng mL^{-1}. All samples underwent two treatments: (1) a 1 mL aliquot was sampled, filtered, and analysed immediately via direct injection (i.e. with no sample preconcentration); and (2) 500 mL was pre-concentrated via solid phase extraction (SPE) using 6 cc Oasis HLB cartridges (Waters) to increase sensitivity. All samples were filtered post-extraction using a 0.22 μm PTFE syringe filter (Phenomenex) and transferred to 1.5 mL glass vials prior to analysis by LC-MS/MS. A procedural blank, instrumental blanks and calibration curves were included with each batch of samples for quality assurance/control purposes. Quantification of target compounds was performed using labelled standards. For further details refer to Supplementary