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A multi-year study of VOC emissions at a chemical waste disposal facility using mobile APCI-MS and LPCI-MS instruments[☆]

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ABSTRACT

Real-time analysis of volatile organic compounds (VOCs) in air is useful both for source identification and emissions compliance applications. In this work, two complementary triple quadrupole mass spectrometers, fitted with an atmospheric pressure chemical ionization (APCI) and a low pressure chemical ionization (LPCI) source, respectively, were deployed simultaneously to investigate emissions of VOCs associated with an Ontario-based chemical waste disposal facility. Mobile measurements performed upwind and downwind of the facility enabled selection of the best locations for stationary sampling. Seven separate field studies were undertaken between 2000 and 2016 to assess how emissions of VOCs have changed at the site as a function of time. Up to twenty-nine VOCs were successfully identified and quantified using MS/MS in each study. Simultaneous deployment of the two mass spectrometers enabled the detection of polar VOCs including alcohols, esters, amines and ketones as well as non-polar aromatic VOCs including benzene and naphthalene in real time. Concentrations of VOCs were found to decrease significantly in the vicinity of the facility over the sixteen year period, in particular since 2007. Concentration values for each year are compared with odour thresholds and provincial guidelines and implications of future expansion of on-site solid waste landfill volumes are also discussed.

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1. Introduction

The necessity to manage industrial and municipal waste with a broad range of physicochemical properties has led to the widespread use of landfill sites globally. Industrial waste can be comprised of organic and inorganic materials in liquid, solid or semi-solid forms. A hazardous waste landfill site may thus contain used oils, cleaning products, pesticides, dioxins, furans, solvents, acids and other materials associated with industrial activities. Storage of these materials can lead to the release of volatile organic compounds (VOCs) to the air, and landfill sites are often associated with emissions of malodorous and toxic organics (Shusterman et al., 1991; Vrijheid, 2000; Kim et al., 2008). VOCs exhibit a wide range of toxicological effects and can contribute to regional-scale production of ground-level ozone and secondary organic aerosols. These secondary pollutants are also of concern from a health perspective (Atkinson, 2000; Heal et al., 2012).

The capacity to detect and quantify VOCs in ambient air in real time is particularly useful for investigating short-lived or intermittent emission events. The advent of on-line mass spectrometers has changed the landscape of air quality compliance work and VOC emission measurements. Traditionally, VOCs are collected in the field in evacuated canisters, sorbent tubes, or in some cases solid phase micro-extraction fibres, and analyzed off-line using gas chromatography-mass spectrometry (GC-MS) (Woolfenden, 1997; Davoli et al., 2003; Durmusoglu et al., 2010; Schuetz et al., 1995). However, these samples provide concentrations for integrated time periods up to several hours in length. This time resolution is often not fine enough for the evaluation of air quality during short-lived emission events.

On-line mass spectrometers are now often favoured for real-time measurements of VOCs in air, with several options available for the ionization of analytes prior to detection (Warneke et al., 2003). Chemical ionization (CI) sources offer an advantage over

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electron ionization sources by producing analyte ions with less excess energy, thus minimizing fragmentation (de Hoffmann and Stroobant, 2007). Atmospheric pressure chemical ionization (APCI), involving a corona discharge as the ionization source for example, is particularly useful for ambient air measurements (Carroll et al., 1975; Karellas, 1992). With APCI-MS, the disadvantage of ion losses during transmission from the source region to the lower pressure MS region are offset by the overall higher ion yield achieved through thermal stabilization at atmospheric pressure (de Hoffmann and Stroobant, 2007). Although the most common use of APCI-MS continues to be detection for liquid chromatography applications, the technique has also proven to be a valuable tool for the direct measurement of VOCs in air (Karellas et al., 2003; Mickunas et al., 1995; Badjagbo et al., 2009).

By flowing ambient air containing VOCs through an APCI corona discharge source region, CI can be achieved using different reagent ions. Water, which is naturally present in the ambient air being analyzed, is a useful reagent for the detection of polar VOCs such as carbonyls and alcohols. This is because their high proton affinity allows for effective proton transfer from hydronium ions, resulting in efficient non-dissociative or “soft” ionization of the analytes (Lindinger et al., 1998). Ammonia also represents a useful alternative CI reagent gas for the detection of aliphatic amines in air. However, APCI-MS techniques exhibit relatively poor sensitivity for aromatic VOCs, such as benzene and toluene. An alternative low pressure chemical ionization (LPCI) source, based on glow discharge, is more suitable for the ionization and detection of trace level aromatics in air (Chen et al., 2006). In this case, charge transfer reactions with ions (N_2^+ , O_2^+ and NO^+) generated from ambient air result in the formation of VOC analyte molecular ions that are subsequently transmitted to the MS for quantification.

Irrespective of whether APCI or LPCI sources are involved, triple quadrupole mass spectrometers can be applied for the detection and quantification of VOCs through MS/MS. Typically, molecular ions are selected in the first quadrupole (Q1) and subsequently undergo collision induced dissociation (CID) with a chemically inert gas, for example argon, in a collisional cell (Q2) to produce product ions with fragmentation patterns that are relatively unique to each analyte VOC. These product ions are then detected in the third quadrupole (Q3). Calibrations and on-site quantification can be performed using precursor/product ion pairs for selected analyte VOCs (Chen et al., 2002).

More recent advances in the field of mobile mass spectrometry include the development and deployment of the membrane introduction mass spectrometer (MIMS), used to quantify VOCs and semi-volatile organic compounds (SVOCs) in ambient air (Bell et al., 2015). This instrument involves the use of a polydimethylsiloxane tube to allow diffusive transfer of VOCs/SVOCs to the ionization region of an ion trap mass spectrometer where electron ionization is performed. MS/MS analysis can be used for quantification while mobile, and this data can be combined with concurrent GPS coordinate measurements to produce spatial maps of VOC/SVOC concentrations in the vicinity of emission sources (Davey et al., 2014; Mach et al., 2015). Other advances include the development of mobile mass spectrometers fitted with desorption electrospray ionization sources (O’Leary et al., 2015), and flexible portable mass spectrometers featuring interchangeable sources for forensic screening (Lawton et al., 2017). Mobile proton transfer mass spectrometers (PTR-MS) have also been deployed for mapping concentrations of VOCs in air quality and point source studies (Wang et al., 2009; Warneke et al., 2014).

In this work, seven separate field surveys employing real time mass spectrometry, carried out between 2000 and 2016, were undertaken to investigate how VOC emissions associated with a large chemical waste disposal landfill and incinerator facility in Ontario

have changed as a function of time. The first surveys were carried out because of complaints regarding odours after the landfill operation was expanded in the late 1990s. The facility emits approximately 50 tonnes of total VOCs per year, including substituted aromatics, alcohols, ketones and amines (Environment Canada: National Pollutant Release Inventory, 2015). Changes in ambient concentrations of a range of VOCs measured downwind of the facility over the sixteen year period are discussed in the context of relevant minimum odour thresholds and current Ontario provincial guidelines. The impact of reduced solid waste landfill space at the facility in recent years is also discussed.

2. Experimental

2.1. APCI-MS

The first Ontario Ministry of the Environment and Climate Change (MOECC) trace atmospheric gas analyzer (TAGA) vehicle is a truck containing a ThermoFisher Scientific TSQ triple quadrupole mass spectrometer, fitted with an APCI source (Fig. 1). The truck also contains a telescopic 10 m meteorological tower for the collection of temperature, wind speed and direction data. Wind direction data are particularly useful for assigning elevated VOC concentrations with specific facilities. The instrument features a modified source region, adapted for the direct measurement of ambient VOCs in air (Karellas et al., 2003). Chemical ionization of VOCs proceeds at atmospheric pressure via proton transfer from hydronium ions produced from the natural water vapour in air using a corona discharge produced by applying a high voltage to a stainless steel needle (5000 V). The ion transfer tube is held at a temperature of 275 °C. Ambient air is drawn through the source region from outside the vehicle at 90 L min⁻¹ continuous flow via a stainless steel and glass tube to minimize VOC residence time prior to detection. The air flow is not dried.

The APCI-MS can be operated in full-scan mode (5 s per scan), where the first quadrupole (Q1) is used to scan through ions in a given m/z range. In this mode, VOCs are typically detected in the form $[M+H]^+$ with minimal fragmentation. In this study, all species quantified by APCI-MS were detected in the form $[M+H]^+$, and these molecular ions were subjected to MS/MS for quantification. The instrument can also be operated in multiple reaction monitoring (MRM) mode, where precursor/product ion pairs associated with specific VOCs are cycled through during each scan. Collision induced dissociation is performed at 25 eV for all compounds. MRM mode is used for quantitation in all cases, and five-point precursor/product ion calibrations are performed prior to each survey using VOC gas standards introduced over a range of concentrations directly into the air flow to the source region. An example of a calibration for butyl acetate using three different product ions is provided in Fig. S1 of the Supporting Information document. Calibration regressions are forced through zero and two (or three where possible) ions are used to calculate concentration data for each VOC. The final reported concentration numbers are calculated as the mean of the values determined for each ion. Calibrations were performed prior to each survey each year. The precision of the APCI-MS is <5% for the species quantified in this work. A new atmospheric pressure photoionization (APPI) source is also currently being tested for the TSQ instrument, to potentially expand its capacity to also quantify aromatic non-polar compounds.

2.2. LPCI-MS

The second TAGA vehicle is a van housing a Sciex IIe MS/MS triple quadrupole mass spectrometer fitted with an LPCI source (Fig. 1) (Karellas and Chen, 2013). The source is operated at

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