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Real time measurement of transient event emissions of air toxics by tomographic remote sensing in tandem with mobile monitoring

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HIGHLIGHTS

- CAT scans of hazardous air pollutants were performed based on long path DOAS.
- Large nocturnal plumes of toluene and xylenes from railcars were detected.
- Mobile PTR-MS measurements confirmed the plumes observed by CAT scans.
- Inverse modeling of fugitive emissions was based on PTR-MS and CAT scan measurements.
- Fugitive emissions inferred from the two data sources were comparable.

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ABSTRACT

During the Benzene and other Toxics Exposure (BEE-TEX) study, a remote sensing network based on long path Differential Optical Absorption Spectroscopy (DOAS) was set up in the Manchester neighborhood beside the Ship Channel of Houston, Texas in order to perform Computer Aided Tomography (CAT) scans of hazardous air pollutants. On 18–19 February 2015, the CAT scan network detected large nocturnal plumes of toluene and xylenes most likely associated with railcar loading and unloading operations at Ship Channel petrochemical facilities. The presence of such plumes during railcar operations was confirmed by a mobile laboratory equipped with a Proton Transfer Reaction—Mass Spectrometer (PTR-MS), which measured transient peaks of toluene and C_2-benzenes of 50 ppb and 57 ppb respectively around 4 a.m. LST on 19 February 2015. Plume reconstruction and source attribution were performed using the 4D variational data assimilation technique and a 3D micro-scale forward and adjoint air quality model based on both tomographic and PTR-MS data. Inverse model estimates of fugitive emissions associated with railcar transfer emissions ranged from 2.0 to 8.2 kg/hr for toluene and from 2.2 to 3.5 kg/hr for xylenes in the early morning of 19 February 2015.

1. Introduction

Measurements of VOC emissions from industry are rarely performed outside the confines of industrial facilities due to the lack of technology beyond immediate source sampling and short-range optical techniques. Because of the rarity of measurements, the general practice today is to calculate emissions based on emission factors or other engineering estimates with apparently large discrepancies (order of magnitude). Methods that enable independent confirmation of emissions estimated by industry at the level of individual emission points, rather than broader facility-wide emission inventories, are increasingly necessary to protect the environment and human health, especially when industrial facilities are adjacent to so-called “fence line communities” or residential areas. This paper is the latest in a series of studies that demonstrate the combination of micro-scale inverse modeling and novel real-time measurement techniques to quantify transient

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releases of pollutants from specific emission points in an industrial facility while operating *outside facility fence lines*.

Olaguer (2013) employed the HARC micro-scale forward and adjoint air quality model to infer formaldehyde and olefin emissions from an olefin flare during the 2006 Second Texas Air Quality Study (TexAQS II) based on Hantzsch fluorescence and automated gas chromatograph measurements approximately 8 km downwind of the emitting facility. The inferred event emissions were consistent with those derived from mobile emission flux measurements using the Solar Occultation Flux (SOF) and *passive* Differential Optical Absorption Spectroscopy (DOAS) techniques.

Buzcu-Guven et al. (2013) applied the HARC model to perform source attribution of benzene based on mobile Proton Transfer Reaction—Mass Spectrometry (PTR-MS; De Gouw and Warneke, 2007) measurements outside an industrial complex in Texas City, Texas during the 2009 Study of Houston Atmospheric Radical Precursors (SHARP). Their inferred benzene emissions were strongly supported by corresponding source attribution results based on Positive Matrix Factorization (PMF).

Olaguer et al. (2013) performed a similar source attribution of formaldehyde and sulfur dioxide based on mobile Quantum Cascade Laser (QCL) and pulsed fluorescence measurements during SHARP. Again using the HARC model, they inferred a formaldehyde emission flux of 18 kg/hr from a Fluidized Catalytic Cracking Unity (FCCU) at one of the largest refineries in the United States. This estimate agreed very closely with simultaneous and independent remote sensing measurements based on *passive* Imaging and Multi-Axis DOAS. In addition, their inferred HCHO-to-SO_2 molar emission ratio was similar to that computed directly from ambient measurements during the release.

In this paper, we apply the micro-scale inverse modeling technique to both mobile PTR-MS and *active* long-path DOAS measurements that were made during the 2015 Benzene and other Toxics Exposure Study (BEE-TEX).

2. The BEE-TEX field study

BEE-TEX was an experimental campaign conducted in the vicinity of the Ship Channel of Houston, Texas during February 2015. The experiment was conceived by the Houston Advanced Research Center (HARC) and implemented by HARC, the University of California at Los Angeles (UCLA), the University of North Carolina (UNC) at Chapel Hill, and Aerodyne Research, Inc. (Aerodyne), with ancillary participation by the University of Houston (UH), Rice University, and Houston Regional Monitoring (HRM) Corp. The goal of BEE-TEX was to facilitate the establishment of state-of-the-art, neighborhood-scale monitoring networks in areas of suspected toxic emissions. The technical objectives of the study included: 1) the demonstration of tomographic remote sensing based on a novel implementation of DOAS as a viable technology for routine area-wide monitoring of hazardous air pollutants, especially in industrial fence line communities, and 2) source attribution and quantification of toxic air emissions based on either tomographic or mobile real time measurements obtained outside the fence lines of industrial facilities. A third objective, which will not be further discussed here, was the demonstration of the utility of cultured human lung cells as indicators of human exposure to air toxics based on cell releases of enzymes and proteins, as well as genetic signals, in response to ambient air pollution (Olaguer, 2015; Vizuete et al., 2016).

The details of the long path (LP-) DOAS instrumental technique as implemented by UCLA are discussed in a companion paper by Stutz et al. (2016), including preliminary tests of the field study instruments at a refinery in Carson, California prior to BEE-TEX. The main innovation consisted of using dual Light Emitting Diodes (LEDs) as UV radiation sources for the measurement of aromatic species, including the so-called BTEX compounds (benzene, toluene, ethyl benzene and xylenes). Computer Aided Tomography (CAT) based on DOAS was previously discussed in anticipation of BEE-TEX by Olaguer (2011), who demonstrated how 3D Eulerian model-based plume reconstruction and source attribution (including emissions quantification) can be performed using the 4D variational data (4Dvar) assimilation technique based on measured path average concentrations. Olaguer (2011) used training data to show the superiority of the CAT-4Dvar method over the standard Algebraic Reconstruction Technique (ART; Gordon et al., 1970; Todd and Leith, 1990). Olaguer's CAT-4Dvar method was used as the basis of *post hoc* plume reconstruction and source attribution during BEE-TEX in addition to routine real time CAT plume reconstruction using ART.

Areal DOAS CAT scans were complemented by real time in situ monitoring based on three mobile platforms, each equipped with a PTR-MS, a global positioning system, and portable meteorological instruments. One of these mobile laboratories was operated by HARC, and was described in detail by Olaguer et al. (2016a), while another was operated by Aerodyne (Herndon et al., 2005; Yacovitch et al., 2015). The Aerodyne mobile lab was equipped with other real time monitoring devices, including QCLs, and an alternative NO^+ ion source for the PTR-MS, which normally uses hydronium (H_3O^+) as a reagent ion. A third mobile laboratory was operated by UH in stationary mode throughout the entire BEE-TEX campaign, mainly to provide PTR-MS data for inter-comparison with LP-DOAS measurements (Stutz et al., 2016) and correlation with lung cell exposures (Vizuete et al., 2016), including measurements of non-HAP species.

The main air toxics monitored by PTR-MS were benzene, toluene, C_2-benzenes (ethyl benzene and xylenes), and styrene. In addition, the Aerodyne PTR-MS measured 1,3-butadiene using NO^+ as a reagent ion, while formaldehyde (HCHO) was measured by a QCL. Olaguer et al. (2016b) discussed the operation of the HARC PTR-MS during BEE-TEX, including calibration and inter-comparison with the PTR-MS instruments on-board the two other mobile laboratories. In addition, they analyzed measurements of benzene plumes associated with pipeline leaks in Galena Park, Texas on the north shore of the Houston Ship Channel, where several marine port facilities are located.

In this paper, we concentrate primarily on BTEX compounds. BTEX monitoring data from the HARC mobile laboratory and the DOAS CAT scan network, including the results of the ART plume reconstruction, were broadcast in real time via a Web site visible only to selected field study participants, as described by Olaguer (2015) and Olaguer et al. (2016a,b). This enabled adaptive measurements to be made fairly quickly in response to observed large plumes and associated emission events. The discoveries discussed here were the fruit of this real time monitoring strategy. Further details of the measurements and data interpretation are described below.

3. CAT-DOAS network configuration and measurements

Details of the CAT-DOAS network are discussed in the companion paper by Stutz et al. (2016). Briefly, the CAT-DOAS network was set up in the Manchester neighborhood of Houston beside the Ship Channel, close to a major refinery as indicated in Fig. 1, which shows the configuration of DOAS light paths. The LED light sources and DOAS detectors were mounted on scaffolding towers at Hartman Park and Manchester St., the latter site just across the main entrance of the refinery. Reflectors were mounted on the Hartman Park scaffolding tower, on guard rails of the IH610 Bridge connecting Manchester to the Galena Park neighborhood across the