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Tracking hazardous air pollutants from a refinery fire by applying on-line and off-line air monitoring and back trajectory modeling☆

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HIGHLIGHTS

- An industrial fire can emit hazardous air pollutants into the surrounding areas.
- Both on- and off-line monitoring are needed to study air pollution from fires.
- Back trajectory and dispersion modeling can trace emission sources of fire-related pollution.

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ABSTRACT

The air monitors used by most regulatory authorities are designed to track the daily emissions of conventional pollutants and are not well suited for measuring hazardous air pollutants that are released from accidents such as refinery fires. By applying a wide variety of air-monitoring systems, including on-line Fourier transform infrared spectroscopy, gas chromatography with a flame ionization detector, and off-line gas chromatography–mass spectrometry for measuring hazardous air pollutants during and after a fire at a petrochemical complex in central Taiwan on May 12, 2011, we were able to detect significantly higher levels of combustion-related gaseous and particulate pollutants, refinery-related hydrocarbons, and chlorinated hydrocarbons, such as 1,2-dichloroethane, vinyl chloride monomer, and dichloromethane, inside the complex and 10 km downwind from the fire than those measured during the normal operation periods. Both back trajectories and dispersion models further confirmed that high levels of hazardous air pollutants in the neighboring communities were carried by air mass flown from the 22 plants that were shut down by the fire. This study demonstrates that hazardous air pollutants from industrial accidents can successfully be identified and traced back to their emission sources by applying a timely and comprehensive air-monitoring campaign and back trajectory air flow models.

1. Introduction

The production and use of chemicals is predicted to increase worldwide, especially in developing countries and areas in which the economy is in transition and where increased chemical extraction, processing, and use is closely tied to economic development. Although the release of chemicals from industrial processes is carefully regulated to prevent any harm to people and the environment, it is more difficult to control accidental releases from chemical accidents such as explosions, gas or vapor leaks, fires, and spills of liquids or solids [1]. Despite an increased understanding of how accidents occur in the chemical processing industry, today's safety measures and indicators do not completely prevent these types of accidents from occurring [2]. Health risks from toxic emissions after major disasters, such as the chemical accidents in Seveso, Bhopal, and Formosa [3–6], have caused public health concerns for the residents and survivors in the disaster-affected areas [7]. Empirical evidence linking such incidents to toxic emissions is usually hampered by difficulties in identifying the actual status of the environmental contamination after the accidents in a timely fashion. The lack of timely and sufficient environmental monitoring immediately after such incidents is a major obstacle to conducting sound health risk assessments of population exposures [8]. The advancement of air-monitoring techniques in recent years includes on-line remote sensors of open-path Fourier transform infrared spectroscopy (OP-FTIR) [9–11] with a differential optical absorption spectrometer (DOAS) [12,13], on-line gas chromatography systems [14–17], and off-line sampling canisters with gas chromatography–mass spectrometry (GC–MS) [18,19], which have overcome existing technical barriers and have made it possible for

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researchers to conduct comprehensive assessments of air pollution following disasters.

The No. 6 Naphtha Cracking Complex is situated in Mailiao Township in central Taiwan and is owned by the Formosa Petrochemical Corporation. It is a major production facility for fuels and chemicals in Taiwan. Since the complex began operation in 1996, a total of 21 major accidents have been documented by the Environmental Protection Bureau of Yunlin County at the No. 6 Naphtha Cracking Complex. In most cases, the air pollution status of the surrounding area was not successfully determined by the regulatory authorities after these accidents due to limited air-monitoring capabilities.

One notable exception was the large fire incident that occurred on May 12, 2011, which we use to demonstrate how we successfully quantified hazardous air pollutant levels from the plant by partnering with regulatory authorities and applying a wide variety of air-monitoring systems, including an existing air-monitoring network, on-line Fourier transform infrared spectroscopy (FTIR), off-line GC–MS, and a portable meteorological station to measure hazardous air pollutants during and after the accident.

2. Materials and methods

2.1. Study areas

As shown in Fig. 1(a), the No. 6 Naphtha Cracking Complex is situated on the west coast of central Taiwan in Mailiao Township, Yunling County, Taiwan, comprising a total area of 2603 ha. This facility houses 64 plants within a single complex, including oil refineries, naphtha cracking plants, co-generation plants, coal-fired power plants, heavy machinery plants, boiler plants, and downstream petrochemical-related plants [20]. As shown in Fig. 1(b), Mailiao Township (to its east) and Taishi Township (to its south) are 2 neighboring areas of this complex, which together contained approximately 61,600 residents within a total area of 134 km^2 as of 2012 [21]. Various air quality-monitoring sites within these 2 townships that provide air pollution data for tracing hazardous air pollutants from the complex to the neighboring areas are also shown in Fig. 1(b).

2.2. The fire on May 12, 2011

At 20:40 p.m. on Thursday, May 12, 2011, there was a large fire at the No. 6 Naphtha Cracking Complex. The fire was caused by a liquefied petroleum gas (LPG) fuel leak, which consisted of 50% propane and 50% butane escaping from the pipelines. The fire was extinguished at 5:45 a.m. on Friday, May 13, 2011. This accident forced 22 plants near the fire or that were fueled by LPG to immediately shut down their production facilities. The raw materials and major products from the 22 affected chemical plants that were shut down during the incident are listed in Table 1. These 22 chemical plants include the naphtha cracking plant 1 (OL1), aromatic plant 1 (ARO1), styrene monomer plants 1 and 2 (SM1 and SM2), ethylene vinyl acetate plant (EVA), acrylonitrile plant (AN), high-density polyethylene plant (HDPE), methyl methacrylate plant (MMA), epichlorohydrin plant (ECH), polycarbonate plant (PC), isooctanol plant (2EH), acetic acid plant (AA), C4 olefin plant (C4), vinyl chloride monomer plant (VCM), polystyrene plant (PS), acrylonitrile-butadiene-styrene plant (PS/ABS), ethylene glycol plants 1 and 2 (EG1 and EG2), bisphenol A plants 1 and 2 (BPA1 and BPA2), epoxy resin plant (EPOXY), hydrogen peroxide plant (H2O2), and the 1,4-butylene glycol plant (14BG). The production capacities of these chemicals are in the range of tens to millions of tons per year. After the accident, most of the remaining raw materials and products contained in the pipes and vessels from these plants were transferred to 10 gas flare sets for emergency release, which included AA, AN, ARO, 2EH, EVA, DEHP, OL, PC, PS, and SM and which lasted for 1 day. The locations of these 22 chemical plants, the origin of the fire, the sites of the 10 flares, and the downwind sampling sites around the fire inside the complex are shown in Fig. 1(c).

2.3. Air quality-monitoring methods and locations

2.3.1. Existing air quality-monitoring network

A fixed-site air-monitoring station was previously installed at the Taishi Township Library by the Taiwan Environmental Protection Administration (TEPA) in 1993 (http://taqm.epa.gov.tw/taqm/en/b0101.aspx). Air quality monitors were installed on the roof of the building, and the roof is approximately 11 m high with air inlets at approximately 4.5 m above the roof. This station was the only air-monitoring post near the complex that was available for evaluating the emissions of pollutants of interest and their contribution to the deterioration of air quality for the approximately 61,600 residents of Mailiao and Taishi (over an area of 134 km^2) in 2012 [21]. Hourly concentrations were continuously measured at the Taishi station using a flame ionization detector for total hydrocarbons (THC) and nonmethane hydrocarbons (NMHC), a non-dispersed infrared adsorption analyzer for carbon monoxide (CO), an ultraviolet fluorescence analyzer for sulfur dioxide (SO_2), chemiluminescence for nitrogen monoxide (NO) and nitrogen dioxide (NO_2), and a β-ray attenuation method for PM_{10}. The hourly wind speeds and wind direction were also measured at this fixed-site monitoring station. The hourly wind speeds were measured with cup anemometers (Model 014A, Met One Instruments, Inc., Grants Pass, USA), and the wind direction was measured using a wind vane (Met-One Model 024A, Met One Instruments, Inc., Grants Pass, USA).

TEPA also set up a Photochemical Assessment Monitoring Station (PAMS) at the Taishi Township Library to measure the hourly concentrations of 56 hydrocarbons (http://taqm.epa.gov.tw/taqm/en/b0104-4.aspx), including C_2–C_{12} alkanes, alkenes, and aromatics, with an on-line gas chromatograph-flame ionization detector (auto GC/dual FID, PerkinElmer, USA) beginning in May 2007. More details concerning the on-line GC-FID system, the VOC analyses, and the quality control and assurance procedures have been provided in previous publications [22,23].

2.3.2. Improved air-monitoring campaign

A variety of air-monitoring instruments were deployed before and during the accident to evaluate the air toxin levels inside and downwind of the complex.

2.3.2.1. Canisters with GC/MS around the fire. Volatile organic compound (VOC) monitoring was performed using the 6 L fused silica-lined canister sampling technique (Model 29-10622G, Entech Instruments, Inc., Simi Valley, CA, USA) with a pre-concentration system (Entech 7100 cryogenic sample pre-concentrator, Entech Instruments, Inc.) and GC–MS (Agilent 7890A GC and 5975C MS, Agilent Technologies, Inc., Santa Clara, CA, USA) to trace the levels of hazardous air pollutants inside the complex immediately after the fire. Spot air samples were collected from 5 locations downwind of the fire from 21:20 to 23:30 on May 13, 2011 and were later analyzed using the US EPA TO-15 method [24] to quantify certain potential hazardous air pollutants related to the fire, such as vinyl chloride, 1,2-dichloroethane, 1,3-butadiene, acrylonitrile, and vinyl acetate, which were not readily measured by the PAMS.

2.3.2.2. Mobile PAMS and OP-FTIR at downwind locations. A mobile Photochemical Assessment Monitoring Station (MPAMS) was moved to Mailiao Elementary School in the Haifong District to