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A novel assessment of odor sources using instrumental analysis combined with resident monitoring records for an industrial area in Korea

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HIGHLIGHTS

- We make an attempt novel assessment for characteristics of odorants in industrial area.
- The concentration of RSCs was significantly higher than other odorous compounds.
- The offensive odors in residential area were characterized as 'burned' and 'other' smells.
- We confirm a strong correlation between instrumental analysis and resident monitoring data.
- Resident monitoring data can be used effectively to evaluate the characteristic of odorants emitted in industrial area.

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ABSTRACT

The residents living nearby the Sa-sang industrial area (SSIA) continuously were damaged by odorous pollution since 1990s. We determined the concentrations of reduced sulfur compounds (RSCs) [hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS)], nitrogenous compounds (NCs) [ammonia (NH_3) and trimethylamine (TMA)], and carbonyl compounds (CCs) [acetaldehyde and butyraldehyde] by instrumental analysis in the SSIA in Busan, Korea from Jun to Nov, 2011. We determined odor intensity (OI) based on the concentrations of the odorants and resident monitoring records (RMR). The mean concentration of H_2S was 10-times higher than NCs, CCs and the other RSC. The contribution from RSCs to the OI was over 50% at all sites excluding the A-5 (chemical production) site. In particular, A-4 (food production) site showed more than 8-times higher the sum of odor activity value (SOAV) than the other sites. This suggested that the A-4 site was the most malodorous area in the SSIA. From the RMR analysis, the annoyance degree ($OI \geq 2$) was 51.9% in the industrial area. The 'Rotten' smell arising from the RSCs showed the highest frequency (25.3%) while 'Burned' and 'Other' were more frequent than 'Rotten' in the residential area. The correlation between odor index calculated by instrumental analysis and OI from the RMR was analyzed. The Pearson correlation coefficient (r) of the SOAV was the highest at 0.720 ($P < 0.05$), and overall results of coefficient showed a moderately high correlation distribution range (from 0.465 to 0.720). Therefore, the overall results of this research confirm that H_2S emitted from A-4 site including food production causes significant annoyance in the SSIA. We also confirm RMR data can be used effectively to evaluate the characteristic of odorants emitted from the SSIA.

1. Introduction

As a result of recent industrial development, nearby residents are directly and indirectly exposed to air pollutants in various forms in the environment. Especially, air pollution episodes caused

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by odorants are a particularly important pollution phenomenon in the atmospheric environment of a metropolis (Bundy, 1992). Odorants cause serious problems when an industrial complex is located close to a residential area, and some of the odorants emitted from such an industrial area can cause damage to the residential area. In addition, odorants can even be perceived at low threshold levels, and they can have a psychological impact on residents even at very low concentrations (Capelli et al., 2011; Mackie et al., 1998; Kabir and Kim, 2010; Herr et al., 2003). Odor can cause headaches, loss of appetite, gastrointestinal disorders, sleep disturbances, dyspneas, and allergic phenomena, and civil complaints of odors occur frequently (Gostelow et al., 2001; Tsao et al., 2011). Therefore, odorants emitted from industrial areas can lead to a lower overall quality of life and aggravate the health of the residents and have a negative effect on the local economy (Blanes-Vidal et al., 2012). The reduced sulfur compounds (RSCs) including hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) are identified as the major constituents of malodor problems. The government has designated odor management areas to reduce civil complaints of odorants, and the actual odorant emissions in areas where odor concentration is seriously high are periodically investigated (Yu et al., 2009).

The Sa-sang industrial area (SSIA) was completed in 1975, and it is difficult to conduct environmental monitoring in the area because residential, commercial, and industrial zones are so concentrated. In particular, the environmental problem due to the underdeveloped manufacturing industry occupying most of the SSIA is serious. Thus, the Busan government consistently has tried to improve environmental quality, but the incidence rate of odor complaints from various causes has increased every year. An enormous residential area is located in the east of the SSIA. Odorants can easily move to the residential area owing to the westerly winds that prevail in the country. For this reason, there are constant odor complaints registered in the SSIA. This phenomenon increased markedly when residents moved in on a large scale in the early 1990s.

Various aspects must be considered to analyze the cause and characteristics of odorants for the minimization of odor complaints (Emerson and Rajagopal, 2004; Kim et al., 2005). We have to accurately analyze the characteristics of the change in odorants throughout the year because there are numerous facilities that produce odor emissions located close together in the SSIA. Social participation and strong community involvement in detecting odor problems are needed to identify and evaluate odor sources causing irritation in areas surrounding the industrial area (Nicolas et al., 2010). There have been many recent studies employing social participation and questionnaires to evaluate the annoyance caused by odors (Blanes-Vidal et al., 2012; Sucker et al., 2008; Gallego et al., 2008; Susaya et al., 2011a; Heaney et al., 2011; Aatamila et al., 2012).

The objective of this study is to quantify odorants emitted from the SSIA and to identify emissions sources and major odorants in the SSIA. Odorants such as RSCs, nitrogenous compounds (NCs), and carbonyl compounds (CCs) were sampled in the SSIA from June to November 2011, and their concentrations were determined using a gas chromatography (GC). The results were compared with emission standards and odor threshold values (OTVs). While odor activity value (OAV) and odor intensity (OI) were determined based on the odorants concentrations in many other studies (Kim and Park, 2008; Susaya et al., 2011a; Trabue et al., 2011; Seo et al., 2011; Parker et al., 2013), both the odorants concentrations and resident monitoring records (RMR) were used in this study. The concentrations of the odorants determined by the instrumental analysis were also correlated to the OI.

2. Materials and methods

2.1. Sampling sites

Fig. 1 shows a map of the research area. The SSIA is close to a basin and is surrounded by mountains. Measurements were taken from 6 plant sites (A-1–A-6) and from residential areas (B-1–B-3) in the SSIA in Busan, Korea. Three residential areas (B-1–B-3) where odor complaints have been registered are located in the eastern part of the SSIA. Table 1 shows the types of major industry (A-1–A-6), including iron (metal) production, chemical production, food (fish, meat, cakes, and beverages) production, and waste and sewage treatment. Sampling was conducted during summer (Jun–Aug) and autumn (Oct–Nov) in 2011. Measurements were performed daily in the morning (9–11 a.m.), afternoon (2–5 p.m.), and evenings (7–10 p.m.), 20 times each month and a total of 100 times. Table 2 shows the meteorological conditions (temperature, humidity, and wind conditions) at the research area. The wind direction was primarily northwesterly (WNW, NW, and NNW).

2.2. Instrumental operation

The offensive odor prevention Law was implemented by the Korean Ministry of environment in 2004 in order to manage odors efficiently, and 22 substances have been designated as representative offensive odorants (KMOE, 2007a,b; Seo et al., 2011). In this study, among the representative offensive odorants measured were NCs including ammonia (NH_3) and trimethylamine (TMA), which is known to cause a fishy smell at very low concentrations (Mushiroda et al., 1999; Zhang et al., 2005; Rappert and Muller, 2005), and RSCs including H_2S, CH_3SH, DMS, and DMDS. The CCs including acetaldehyde and butyraldehyde were also monitored.

For NH_3, sodium nitroprusside and sodium hypochlorite were added to the samples and analyzed at 640 nm (range: 190–1100 nm) using a UV/vis spectrophotometer (Shimadzu, UV-1700, Japan) based on the indophenols method (Seo et al., 2011). The aldehyde composition collected from the DNPH cartridge was analyzed by high performance liquid chromatography (HPLC) (Varian, Pro Star 210, USA). Samples were eluted with 70% acetonitrile at 1.0 mL min^{-1} and the converted concentration was measured using 20-μl samples with HPLC. A non-polar octadecyl silane (ODS) column was used for effective detection of different fractions and had an inside diameter of 4.6 mm and a length of 250 mm. RSCs samples were collected using tedlar bags (10 L, TDC, Japan) at 0.5 L min^{-1} using vacuum suction equipment over 10 min after nitrogen gas of high purity (99.99%) had been used to clean the sampling bag five times. The samples were analyzed by GC/PFPD (Varian, GC CP-3800, USA). The column used for separation of the sample was a CP-SIL 5CB LOW Bleed/MS (60 m × 0.25 mm, 1.0 μm). The quantification methods used a cold trap and chromatography/capillary column at 150 °C and the flux of the column was regulated to 2 mL min^{-1} and the temperature of the detector was at 250 °C (Micone and Guy, 2007). The TMA was analyzed using GC-NPD (Shimadzu, GC-14B, Japan) with a column whose flux was set to 2 mL min^{-1} and at 30 °C for 15 min for adsorption and 260 °C for 3 min for desorption (Chien et al., 2000).

Table 3 shows the relative standard error (RSE) and the minimum detection limit (MDL) for quality assurance (QA) of the analytical chemistry. With respect to instrumental precision, the RSE values were calculated based on five repeated analyses with $r^2 > 0.989$ and the values were 0.25 (TMA) to 5.40 (NH_3), and the MDL values described in Table 3 and all of the MDL values of compounds were lower than the emission standard value in Korea.