Technical Note

A Feasible Approach to Quantify Fugitive VOCs from Petrochemical Processes by Integrating Open-Path Fourier Transform Infrared Spectrometry Measurements and Industrial Source Complex (ISC) Dispersion Model

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ABSTRACT

Fugitive emissions are one of the largest sources of volatile organic compounds (VOCs) from petrochemical and chemical plants. However, how to quantify the total fugitive VOC emissions from numerous and mostly inaccessible sources is a time consuming and costly task. This study presents a feasible approach to quantify the fugitive VOC emissions by integrating OPFTIR measurements and the well-developed Industrial Source Complex Short Term Model (ISCST3). A mobile OPFTIR system was set up for 190 hours in the downwind location of a 1,3-butadiene manufacturing process, which has unidentified fugitive sources and should be responsible for the elevated atmospheric 1,3-butadiene concentrations. Wind speeds and directions were found to be the most important factors in the dispersion of the emissions. Therefore, when using trial and error to predict the fugitive 1,3-butadiene emission rates, we divided the field measurement data based on the wind directions and excluded that obtained during lower wind speeds. Then the correlation coefficients between the field data (from the mobile OPFTIR system) and the modeling data (from the ISCST3) were found to be up to 0.529, and the slope of the correlation equation was close to unity. Therefore, integrating the OPFTIR measurement and ISCST3 is a feasible approach to predict the amount of fugitive VOC emissions.

Keywords: Fugitive emissions; VOCs; OPFTIR; ISCST3.

INTRODUCTION

Various air pollutants are emitted through the operation of petrochemical plants, such as highly reactive hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). Pollutant emissions from stacks can be quantified by the flow rate of flue gases and pollutant concentrations in stack flue gases, which are obtained by instrumental samplings or direct measurements. However, pollutants emitted from widely dispersed sources, such as valves, flanges, flares, drains, pump seals, and fittings, generally known as fugitive emissions, are difficult or impractical to measure.

Although the amount of fugitive emissions from a single leaking piece of equipment may be small, the large number of such leaking components makes fugitive emissions the largest source of VOCs from petrochemical and chemical plants, amounting to over a million metric tonnes per year worldwide. In the US, such emissions account for approximately about one third of the total organic emissions from chemical plants. Fugitive VOCs are associated with greater photochemical ozone creation potential (POCP), ozone depletion potential (ODP), global warming potential (GWP), photochemical smog, toxicity, and carcinogenicity. Furthermore, long-term exposure to fugitive pollutants is the most important source of hazard with regard to occupational exposure.

It is important to quantify the total fugitive VOC emissions in order to better deal with the potential environmental hazard that they represent. Fugitive VOC emissions are commonly calculated based on an installed equipment count by equipment type, in conjunction with the corresponding emission factors developed by the US EPA. These emission factors are the averaged amount of volatile organic pollutants emitted per component, or are derived from the measured concentrations for each equipment component. However, the numerous and mostly inaccessible sources of fugitive VOC emissions mean that the related measurement work is costly and time-consuming, and often produces biased

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estimation results .

Open-path Fourier transform infrared (OPFTIR) spectrometry has the advantages of being adaptable, transportable, capable of remotely monitoring several different paths in real time, and carrying out multi-compound analysis without the need to send the samples back to laboratories for chemical analysis. This approach has thus been widely applied for air pollutant monitoring and odor source identification at petrochemical complexes and other large-area sources. Nevertheless, an OPFTIR system cannot obtain information concerning the VOC concentrations and the related emission rates.

The objective of this study was thus to develop a feasible approach to quantify the fugitive VOC emissions by integrating OPFTIR measurement and the well-developed Industrial Source Complex Short Term Model (ISCST3). The emission rates of the fugitive VOCs were estimated by the highest correlation between the field atmospheric VOCs measured by OPFTIR and the modelled data obtained from the ISCST model.

MATERIALS AND METHODS

Strategy for Assessing Emission Rates of Fugitive VOCs from a Specific Source in a Petrochemical Complex

A stationary OPFTIR system was set up beside a petrochemical complex for routine VOC monitoring. When some VOC concentrations were found to be over their regulation levels, the sequential deployment of a pair of mobile OPFTIR systems was carried out at both the upwind and downwind sites of the focal area to identify the VOC emission sources. The detailed deployment strategy used with the mobile OPFTIR systems has been described in our previous study.

The elevated levels of the atmospheric VOC concentrations associated with the fugitive VOC sources are related to the fugitive amounts and weather conditions at the time the leak occurred. Once the sources of VOCs were identified by the mobile OPFTIR systems, and the detected atmospheric VOC concentrations exceeded the related regulation or much greater than that of unaffected ambient air, the dispersion modeling approach was used to predict the emission rates of the fugitive VOCs to the surrounding environment.

The ISCST3 air pollution dispersion model was used in this study, and this has a long history of use and was designated by the US EPA as preferred model for emission sources. ISCST3 is a steady-state Gaussian plume model for continuous source emissions, and can be used to compute the ground-level concentrations from stack, volume and area sources. The vertical and lateral dispersion are estimated using the Pasquill–Gifford curves. The dispersion parameters (such as atmospheric stability and mixing height) adopted in ISCST3 were determined based on the hourly meteorological data obtained from the mobile meteorological observation system deployed at the investigated site.

Description of the OPFTIR Systems

The OPFTIR systems utilized in this study were manufactured by Mastek Technologies, Inc. (Taiwan). Each OPFTIR system consists of an FTIR unit, a retroreflector, and an operational computer. Each FTIR unit was equipped with a mid-band mercury cadmium telluride (MCT) detector, cooled by a liquid nitrogen automatic filling system to maintain the MCT detector below −198°C. Each retroreflector consisted of a corner cube protected by a gold surface, and was mounted on a tripod at the opposite end of the monitoring path. The OPFTIR system was operated by EEL-IRSoft software, which was developed and authorized by the Taiwan Industrial Technology Research Institute, and supplied by Mastek Technologies, Inc.

The operations of the OPFTIR systems and data analyses followed U.S. EPA Method TO-16 and Taiwan EPA Method NIEA A002.10C. The FTIR data were further analyzed by using a multilevel classical least-square (CLS) method. Each spectral data consisted of 64 co-added interferograms, which were recorded every five minutes from 500 to 4500 cm^{-1} at a nominal 1 cm^{-1} resolution. The coefficient of variation of the mobile OPFTIR for standard VOC compounds, including ethyl acetate, 1,3-butadiene, ethylene, 2-butanone, methane and propylene, were between 0.83%–7.2%, while the accuracy were between 90.3%–102%. Furthermore, a mobile meteorological observation system was deployed to record wind speed and direction, as well as temperature, solar irradiance, and relative humidity, to help identify the sources of VOCs.

RESULTS AND DISCUSSION

Regular Monitoring by the Stationary OPFTIR System

After a half year's continuous monitoring, 32 VOCs were detected by the stationary OPFTIR system, including ethylene, ammonia, carbon tetrachloride, propylene, chlorodifluoromethane, dichlorodifluoromethane, vinyl acetate, 1,1,1,2-tetrafluoroethane, 1,2-dichloroethane, methanol, chloroform, 1,3-butadiene, dimethyl ether, ethyl acetate, vinyl chloride, acetylene, cyclohexane, butane, 2-butanone, chloroethane, ethylene oxide, methyl tert-butyl ether, ethanol, isopropanol, dimethoxymethane, isoprene, diisopropyl ether, sulfur hexafluoride, 1,1,1-trifluoroethane, pentafluoroethane, trichlorofluoromethane, and 1,1,2,2-tetrafluoroethane. Among these, 1,3-butadiene, which is used as a monomer in the production of synthetic plastics and rubber, was the most commonly detected VOC that exceeded the air quality regulation of 200 ppb and the odor threshold of 99 ppb. 1,3-butadiene has been classified as a Group 1 carcinogen (carcinogenic to humans) by the International Agency for Research on Cancer. Exposure to 1,3-butadiene is closely associated with an increased cancer risk in hematolymphatic organs, including lymphosarcoma, reticulosarcoma, and leukemia.

After a detailed survey of the raw materials, production processes, intermediate products and emissions that are related to 1,3-butadiene, based on information obtained from the EPA's management database, only a plant with 1,3-butadiene produced in steam cracking by extractive distillation at the petrochemical complex was found out to be the highest potential source of 1,3-butadiene fugitive emissions. In addition, two flares near this plant also emitted 1,3-butadiene

into the atmosphere. The locations of the investigated manufacturing process, flares and the mobile OPFTIR system are depicted in Fig. 1.

Atmospheric 1,3-butadiene Monitoring by a Mobile OPFTIR System

After further investigation, we found that the pipe lines were densely distributed in a square with sides 60 m long, although the whole manufacturing process is situated at a rectangle area that is 115 m in length and 60 m in width (see Fig. 2). A mobile OPFTIR system was set up for 190 hours to monitor the atmospheric 1,3-butadiene concentrations, and this system was located in the downwind direction of the prevailing winds according to the in-situ meteorological conditions, that is, to the south of the 1,3-butadiene manufacturing process. The mobile OPFTIR system was situated at a distance of about 30 meters from the pipeline area.

As illustrated in Fig. 3(a), the wind rose shows that the prevailing wind directions during the monitoring period were basically from the north, including northeast, northwest and west. The pollution rose plot of 1,3-butadiene (Fig. 3(b)) shows that increases in the 1,3-butadiene concentration and detection frequency occurred when the northwest and northeast winds prevailed. When the prevailing winds were blown from the northwest and northeast, the average atmospheric 1,3-butadiene concentration detected by the downwind mobile OPFTIR system was 86.5 ppb, which was approximately 6.4 times higher than when the prevailing winds were blown from the south. Furthermore, even when the speed of the south wind was low or close to calm, the dispersion of the fugitive 1,3-butadiene could still affect the upwind mobile OPFTIR system. This is not only due to the very close distance between the mobile OPFTIR system

and the pipeline area, but also because the evaporative emissions from the 1,3-butadiene production process were significant.

Predicting the Emission Rates of Fugitive 1,3-butadiene by ISCST3

Although the accuracy of ISCST3 with regard to estimating VOC concentrations might be affected by the decay of VOCs in the air due to photolysis, the OPFTIR was situated quite close to the target plant, and hence the time it took the fugitive VOCs to move from the sources to the monitoring line of the OPFTIR would be relatively short. In this context, we assumed the photolysis of VOCs during the transportation period could be negligible.

In order to evaluate the emission quantity of the fugitive 1,3-butadiene, we used ISCST3 to predict the emission rates of the fugitive 1,3-butadiene by assuming different fugitive emission rates of 1,3-butadiene from the manufacturing process. In theory, a very good correlation with regard to the atmospheric 1,3-butadiene concentration could be obtained between the field measurement data (from the mobile OPFTIR system) and the modeling data (from ISCST3), when the assumed fugitive emission rates used in ISCST3 were close enough to the actual ones. We assumed that emissions from a volume source, instead of point or area sources, should be the most correspondent scenario to the real fugitive 1,3-butadiene sources, and thus a volume source of 60 m in length, 60 m in width and 6 m in height was assumed in ISCST3, as shown in Fig. 4.

There are many factors governing pollution dispersion from emission sources, but wind speed and direction have been found to be the most important ones. Therefore, in the first stage of the trial and error process used to predict the fugitive 1,3-butadiene emission rates, we divided the field
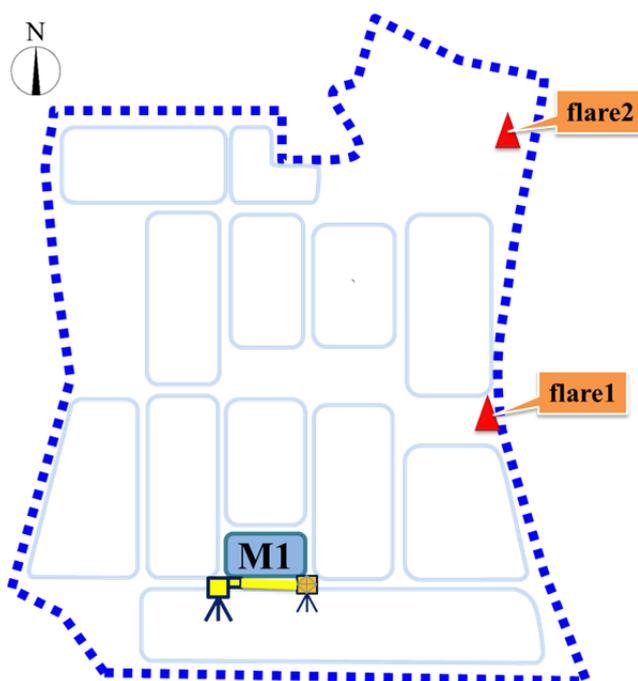
Fig. 1. The locations of the 1,3-butadiene manufacturing process and mobile OPFTIR system in the investigated plant.
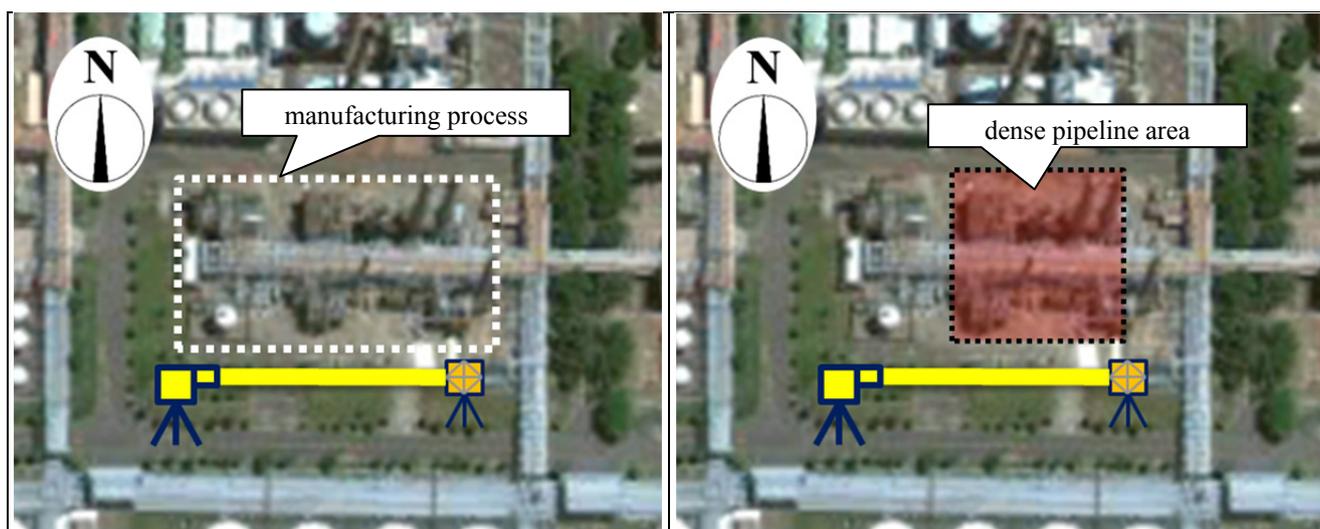
Fig. 2. The dense pipeline area in the investigated manufacturing process.
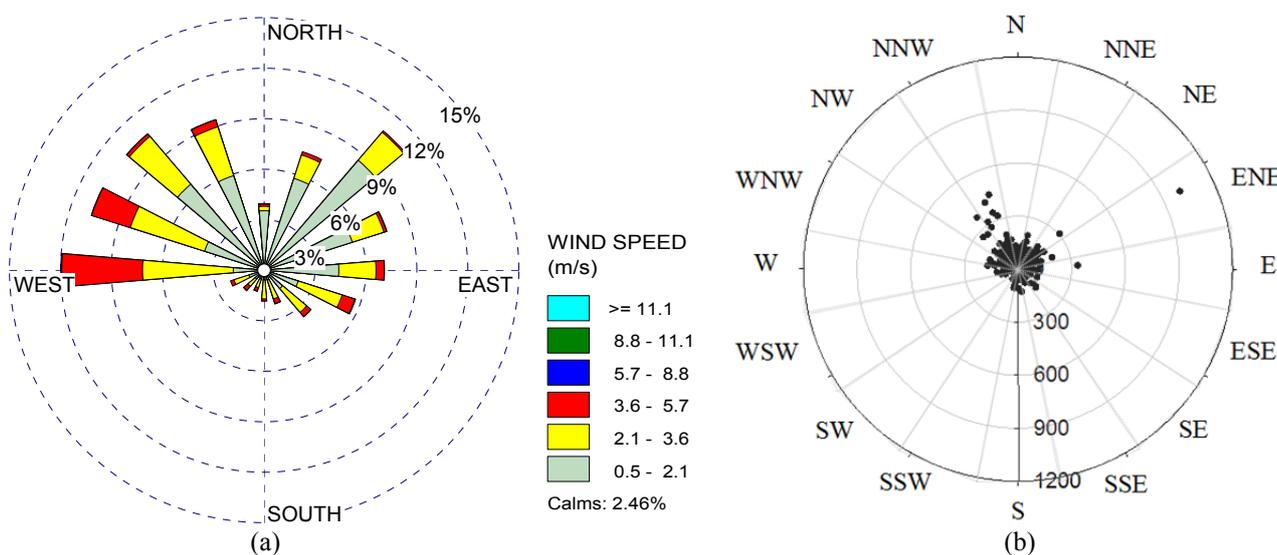

Fig. 3. (a) Wind rose and (b) pollution rose obtained from the mobile OPFTIR system during the monitoring period.
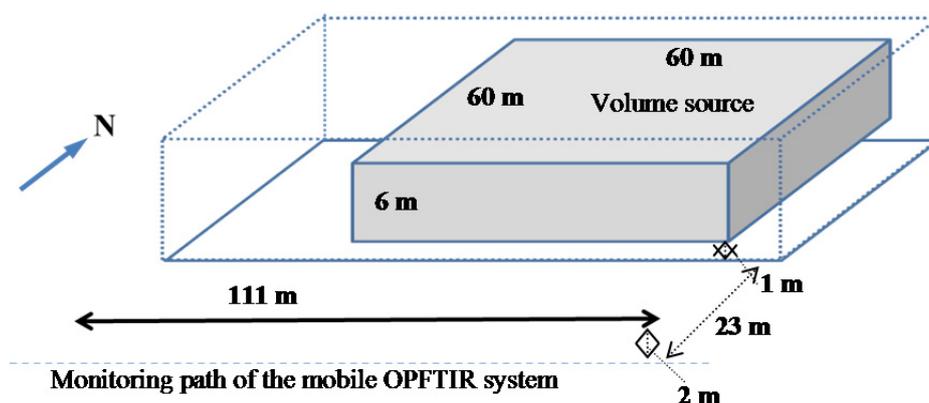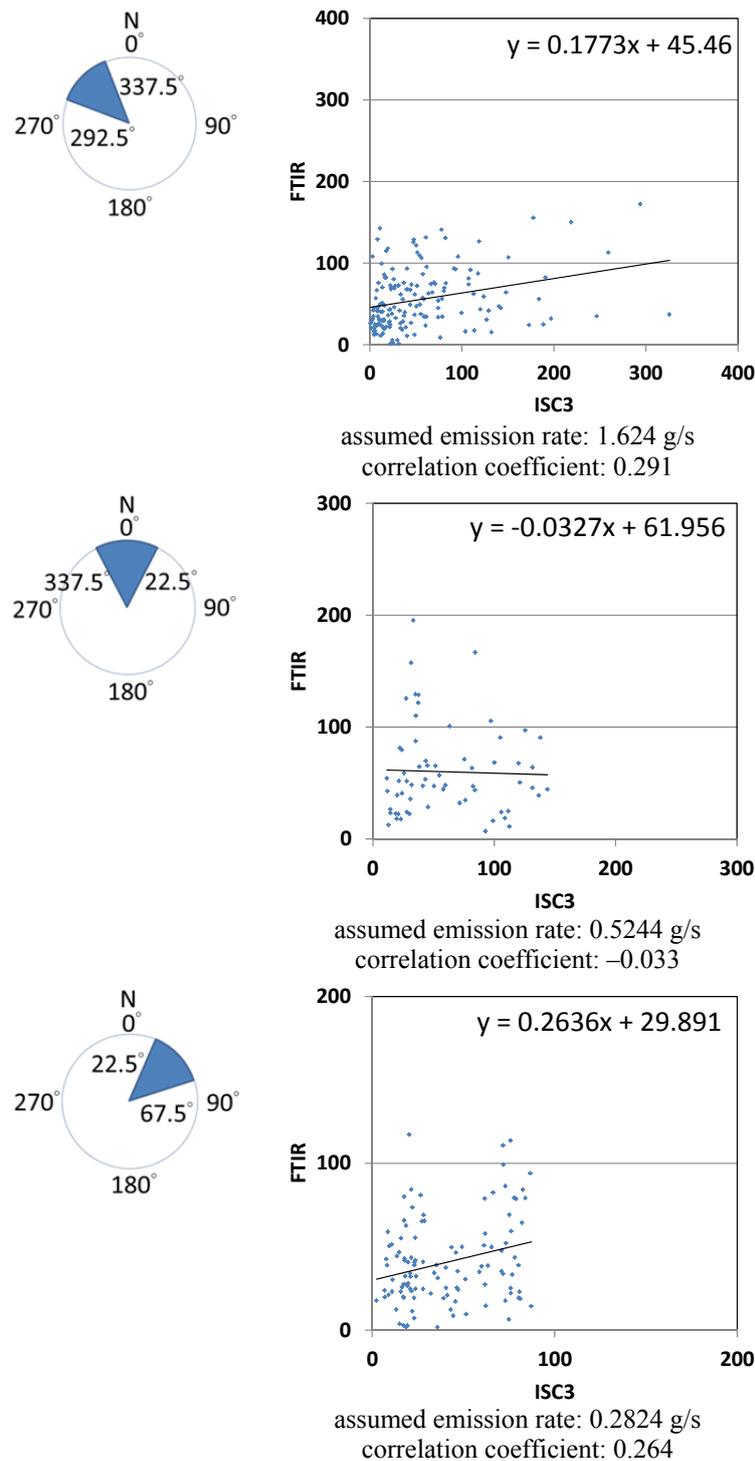

Fig. 4. A volume source with 60 m in the length, 60 m in width and 6 m in height simulated in the ISCST3.

measurement data from the mobile OPFTIR system into three groups based on the wind direction, that is, from the northwest, north, and northeast, because these could directly blow the fugitive 1,3-butadiene across the monitoring path

of the mobile OPFTIR system. Different fugitive 1,3-butadiene emission rates were assumed for each group, and the one that had the highest correlation between the field measurement data (from the mobile OPFTIR system) and the modeling data (from ISCST3) was chosen. The results of this trial and error process, as well as the obtained fugitive 1,3-butadiene emission rates and correlation coefficients, are depicted in Fig. 5. The predicted fugitive 1,3-butadiene

emission rates were 1.624, 0.524 and 0.282 g/s for the northwest, north, and northeast wind directions, but their correlation coefficients were all low, ranging from –0.033 to 0.291. The low correlation coefficients were mainly due to the much lower field measurement data compared to the modeling data, since the slopes of the correlation equations were much lower than unity. This is obviously related to the dispersion of fugitive 1,3-butadiene during the low wind

assumed emission rate: 1.624 g/s
correlation coefficient: 0.291

assumed emission rate: 0.5244 g/s
correlation coefficient: –0.033

assumed emission rate: 0.2824 g/s
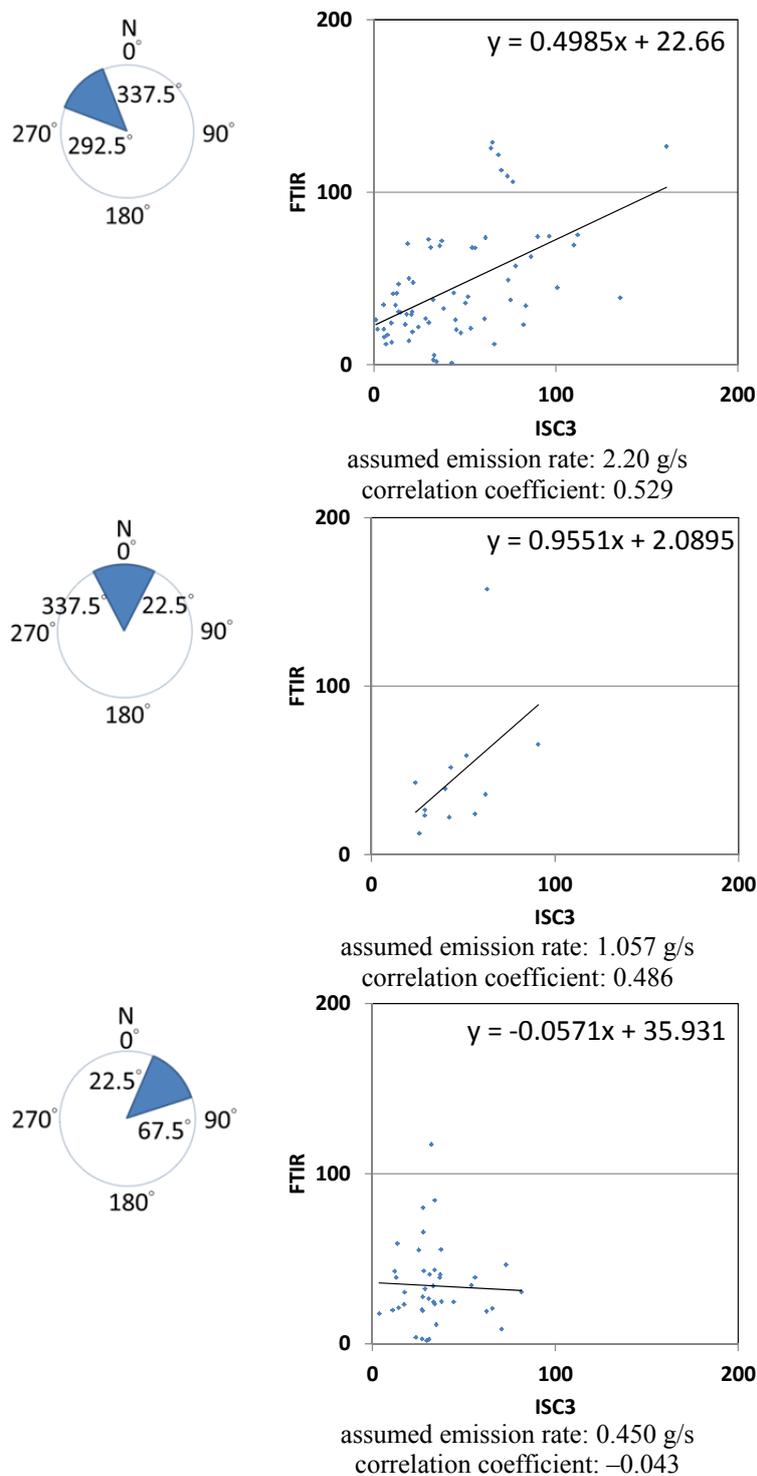correlation coefficient: 0.264

Fig. 5. Estimated 1,3-butadiene emission rates and correlation coefficients of field measurement data and modeling data.

speed periods. In other words, when the speeds of the northern winds became low, the dispersion force can still make the fugitive 1,3-butadiene moving northward, and thus decrease the concentration of 1,3-butadiene detected by the mobile OPFTIR system situated at the downwind location.

Therefore, in the second stage of the trial and error process, the data obtained when the wind speed was lower than 2 m/s were not included in the correlation. Again, the fugitive 1,3-butadiene emission rate that had the highest correlation between the field measurement data and modeling data was chosen. The results of this trial and error process, as well as the obtained fugitive 1,3-butadiene emission rates and correlation coefficients, are depicted in Fig. 6. The predicted fugitive 1,3-butadiene emission rates were 2.20,

assumed emission rate: 2.20 g/s
correlation coefficient: 0.529

assumed emission rate: 1.057 g/s
correlation coefficient: 0.486

assumed emission rate: 0.450 g/s
correlation coefficient: –0.043

Fig. 6. Estimated 1,3-butadiene emission rates and correlation coefficients of field measurements and modeling data (the data obtained for wind speeds lower than 2 m/s were excluded).

1.06 and 0.45 g/s for the northwest, north, and northeast wind directions. The Spearman correlation coefficients increased to 0.529 and 0.486 for data obtained during the northwest and north wind periods, respectively. For the northern wind periods, the slope of the correlation equation ($r = 0.995$) was even very close to unity, revealing that integrating the OPFTIR measurement and ISCST3 to predict the fugitive VOC emissions is a feasible approach. The intercept (2.09 ppb) represents the background atmospheric 1,3-butadiene concentration. The higher intercept (22.60 ppb) found during the northwestern wind period may imply that there were unidentified 1,3-butadiene sources from the northwest. Similarly, the flares located at the northeast may also emit 1,3-butadiene into the atmosphere. The 1,3-butadiene emitted from the flares could be detected by the mobile OPFTIR system during the northeastern wind periods, and thus resulted in a significant difference between the field measurements and modeling data. This is why the correlation was still very low for data obtained during the northeastern wind periods.

CONCLUSIONS

A very good correlation with regard to the atmospheric 1,3-butadiene concentration could be obtained between the field measurements (from the mobile OPFTIR system) and the simulated data (from ISCST3) when the assumed fugitive emission rates used in ISCST3 were close enough to the actual ones. Wind speeds and directions were found to be the most important factors in the dispersion of the emissions. Therefore, when using trial and error to predict the fugitive 1,3-butadiene emission rates, we divided the field measurement data based on the wind directions and excluded that obtained during lower wind speeds. The results showed a moderate correlation between the field measurements and modeling data, and the slope of the correlation equation was close to unity, revealing that integrating OPFTIR measurements and ISCST3 is a feasible approach to predict the quantities of fugitive VOC emissions.

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