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High-density volatile organic compound monitoring network for identifying pollution sources

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Abstract

The elusive sources of air pollution have hampered effective control across all sectors, with long-term consequences for the greenhouse effect and human health. Multiple monitoring systems have been highly desired for locating the sources. However, when faced with extensive sources, diverse air environments and meteorological conditions, the low spatiotemporal resolution, poor reliability and high cost of existing monitors were significant obstacles to their applications. Extending our previous demonstration of sensitive and reliable electrochemical sensors, we here present a machine-learning-assisted sensor arrays for monitoring typical volatile organic compounds (VOCs), which shows the consistent response with gas chromatography-mass spectrometry in the actual air environment. As a proof-of-concept, a low-cost and high resolution VOC network of 152 sets of monitors across ~55 km^2 of mixed-used land is established in southwest Beijing. Benefiting from the strong reliability, the pollution sources are revealed by the VOC network and supported by the joint mobile sampling of a vehicle-mounted gas chromatography-mass spectrometry system. With the sustained help of the network, the sources polluted by the local industrial facilities, traffic, and restaurants are effectively site-specific abatement by the local authorities and enterprises after the next half-year. Our findings open up a promising path toward more effective tracing of regional pollution sources, as well as accelerate the long-term transformation of industry and cities.

Keywords: VOCs, electrochemical sensor array, sensor network, high emission identifications, anthropogenic sources, abatement

1. Introduction

Ambient air pollution emission has caused approximately 4.5 million deaths, huge economic losses and simultaneous high-level CO_2 emissions around the world every year (Forouzanfar et al., 2016; Qian et al., 2021). If the pollution levels are not controlled, global warming would be impossible to keep below 1.5 ℃ and the deaths will reach 6-9 million in 2060 (Landrigan, 2017; Rogelj et al., 2018). Volatile organic compounds (VOCs), as a typical kind of air pollution, have a variety of artificial sources, including residential heating, cooking, industry and traffic (Cai et al., 2019; Lelieveld et al., 2015; Yang et al., 2018). The abundance and spatial distribution of easily diffusible VOCs are mainly controlled by factors of emission rate, pollution source distribution and meteorological conditions, usually are varying widely in concentrations of areas adjacent to the sources (Jobson et al., 1999; Liu et al., 2012). This makes the abatement of VOCs extremely challenging. As a result, recognizing and regulating the site-specific source of VOCs is difficult but crucial for environmental sustainability (Wang et al., 2020).

An increasing number of studies indicated that the concentration and abundance of ambient VOCs can be discriminated by analytical instruments such as gas chromatography-mass spectrometry (GC-MS) and proton transfer reaction time-of-flight mass spectrometer (Cai et al., 2019; Müller et al., 2014; Song et al., 2007). However, due to the high cost, massive resource consumption and complex data processing, it is impossible to apply them in a high-density pattern to timely identify specific sources in the field. The booming of gas sensor technologies such as electrochemistry, photoionization and semiconductor brings bright prospects for solving this problem due to its fast response, low cost, convenience and long-term unsupervised (Bi et al., 2020; Caubel et al., 2019; Mead et al., 2013). However, their low robustness, poor selectivity and insufficient accuracy have led to users' concern about data authenticity (Lewis and Edwards, 2016; Spinelle et al., 2017; Williams, 2019), especially the considerable uncertainty of vast interferents in the atmosphere for ambient VOC monitoring (Esposito et al., 2016; Maag et al., 2018; Van den Broek et al., 2019). In theory, an attractive strategy is to design a circuit that integrates multiple sensors to obtain complicated information about VOCs (Baron and Saffell, 2017; Güntner et al., 2016; Lichtenstein et al., 2014; Mayer and Baeumner, 2019).

Here, we present a monitor by integrating various electrochemical sensor arrays (SAM) with the assistance of a machine-learning algorithm. The SAM is calibrated to monitor total VOC

(TVOC) concentration with similar performance to GC-MS in the atmosphere. Utilizing the SAMs, we have established a large-scale, low-cost and high-resolution TVOC network, covering an area of ~55 km^2 in southwest Beijing. The network displays live TVOC concentration dynamics on fine spatial and temporal scales, effectively reinforcing our understanding of stationary and mobile pollution sources in the city. Furthermore, the vehicle-mounted GC-MS serves as a reliable assistant to investigate the species of VOCs. With the help of SAMs, regulators and enterprises can flexibly formulate emission reduction measures to achieve effective abatement benefits in a short period and sustainable supervision affection. This provides further insight into air pollution mitigation through VOC source monitoring.

2. Materials and Methods

2.1 Development of SAMs

SAMs have been designed by integrating technologies of nanomaterials, screen-printed electrodes and integrated circuits (**Fig. 1a**) and can carry up to ten sensors. They featured a sensor module array with various chips with high sensitivity, selectivity and stability (**Table S1**), a narrowband Internet of Things communication system, lithium-ion batteries and photovoltaic panels. Lithium-ion batteries and photovoltaic panels were applied for the long-term power supply of the sensors and communication modules. The integrated circuits were used for amplification, processing and wireless transmission of the sensor signals (**Fig. 1b**). Specific details on the nanomaterials and sensor fabrication can be found in our previous work and related work (**Table S1**) (Li et al., 2021; Zhang et al.,2021; Zhang et al., 2022; Koziel et al., 2004). The SAMs were compactly integrated into a waterproof and dustproof enclosure, where the external air was transmitted by a diffusion mechanism. The SAMs were inspected and certificated of Explosion-proof Safety and Restriction of Hazardous Substances.

2.2 Calibration of SAMs

Sensors in SAMs were firstly tested by different gases (typical VOCs species: formaldehyde, methanol, toluene, ethylene, isobutene, dimethyldisulphide; and the typical interfering gases: oxygen, nitrogen dioxide, amnion, and hydrogen sulfide) to determine the selectivity. Then they were calibrated by the selected gases from ppb- to ppm- level concentrations to determine the

performance of the SAMs. A neural network algorithm was applied to correct the data of the sensors via comparison test data of GC-MS and sensors (**Fig. S1**). The temperature and humidity sensors were used through the built-in signal processor to compensate for the influence of temperature (from 0 °C to 40 °C) and humidity (from 5%RH to 95%RH) on the sensor readings. Before installation, they were also checked for consistency and long-term stability compared with GC-MS (Agilent 5977b GC/MSD).

2.3 Installation of SAMs

Our study domain was restricted to a mixed land-used zone (including industrial area, residential area and natural area) in southwest Beijing, China. The atmospheric sensor network of 152 sets of SAMs for TVOC monitoring was installed on a ~55-km^2 scale with the help of the local environmental protection agency, local enterprises and residents. The individual SAMs were kept under one kilogram (excluding solar panel) for convenient on-site installation. The overall cost of producing and installing a set of SAM was maintained under $3,000. To keep the electricity supply to SAMs, the photovoltaic panels were placed separately on the sunny side of the building to enhance sunlight reception, while the SAMs were installed in the shade to reduce the effect of illumination. The distribution of SAMs was presented in **Fig. S2**. The distribution was planned to be as homogeneous as possible because the locations largely influence the availability of SAMs. A southern SAM at upwind was set to measure background concentration. The locations were overlapped with Google maps, which displayed road information and land use types. SAMs were fixed to cement poles or steel buildings, about three metres above the ground.

2.4 Data post-process, management and analysis

The SAMs sent monitoring data to the online database every five minutes. The data were also backed up into the Secure Digital Memory Card. The data were programmed and filtered to delete redundant (more than one data sets at the same time) and invalid measurement results. The hourly and daily data averages were calculated. Inaccurate (constant for more than one day) or invalid (the value beyond the detectable range) TVOC concentration data were detected and removed for further analysis. The cluster analysis method was employed to classify and filter-out

abnormal fluctuation of SAMs. Linear Interpolation was used to draw the hourly, daily, or monthly concentration map with Origin's contour function (Data boundary, total points increase factor=200, smoothing parameter=0.001).

2.5 Mobile sampling by vehicle-mounted GC-MS

A high temporal resolution online vehicle-mounted GC-MS (SPIMS 2000, Hexin mass spectrometry) was used to determine the local VOC emission. The vehicle sailed along the highway from 13:00 to 15:30 on 30th August. 33 sets of SAMs (21.7% of all SAMs) were overlapped with the vehicle route (distance less than 20 metres) through longitude and latitude comparison.

3. Results and Discussions

3.1 Reliable SAMs for monitoring TVOCs

SAMs can accurately detect TVOC concentration down to ppb-level. The functional mechanism of the sensors to VOCs is based on the electrocatalytic redox principle (Stetter and Li, 2008) (**Fig. 1c**). **Fig. S1** shows the typical linear amperometric response current of SAMs to the standard gas mixtures of VOCs from 0 to 5000 ppb with the limit of detection of 10 ppb. Comparative indoor or outdoor air tests on dozens of SAMs demonstrate good consistency with a mean absolute percentage error (MAPE) of $10.49 \pm 4.93\%$ (**Fig. S3**). The reliable responsiveness of SAM to TVOCs in complex atmospheric environments is the cornerstone of monitoring. Six SAMs were compared with GC-MS for monitoring TVOCs in the real atmospheric environment (**Fig. 1d, Fig. S4**). The results show a consistent response for three light pollution events of the location (7-11 October & 19-21 October & 10-12 November 2020), indicating good consistency in the dynamic trend between SAMs and GC-MS. The MAPE and coefficient factor (R^2) between SAMs and GC-MS in the field observation are $46.0 \pm 3.0\%$ and 0.74 ± 0.01, respectively. This can be attributed to the different measurement methods and spatiotemporal deviation between SAMs and GC-MS, and trends of exaggerating the error for small values by MAPE. These demonstrate the potential of SAMs for monitoring the atmospheric environment in the real atmospheric environment.

3.2 Establishing a high-resolution SAMs' network

A high-resolution SAMs' network has been successfully established by distributing 152 sets of SAM over a ~55-km^2 area in southwest Beijing (**Fig. 2a**). Views of the installed SAMs are shown in **Fig. 2b-e.** The installation locations were designed to include industrial areas, residential areas, highways and pathways of industrial and residential boundaries, and upwind directions. We classified the deployed SAMs into six categories by the potential sources within 200 metres: Factories (78 points), Factory boundary & highways (24 points), Factory boundary & path (13 points), Highways (15 points), Residential area & path (21 points) and Upwind (1 point). In addition, the SAMs have been examined and certified for Explosion-proof Safety and Restriction of Hazardous Substances to ensure that they meet the requirements for installation in industrial environments.

The SAMs' network collected 90.8% of valid data during the 153-day observation period (from 20th August 2021 to 20th January 2022, from summer to autumn, **Fig. S5**). Lost or abnormal data was mainly contributed by network signal problems or insufficient solar power supply. There was approximately no data loss due to hardware problems of SAMs, which can be attributed to our calibration before installation.

3.3 Tracking pollution sources

The SAMs' network reveals the real-time variability of spatial TVOC concentrations, allowing for the identification of potential pollution sources and the formation process. As shown in **Fig. S6, Fig. S7** and **Video 1**, numerous SAMs of points I to II in the east and west of the domain, near the gate or storage tanks of two factories, exhibit a relatively high concentration (≥700 ppb) mainly from around 0:00 to 8:00 and from Thursday to Sunday. Field investigations reveal that the emission characteristics at point I are primarily caused by truck transit (traffic). The high values at point III, unlike point I, originate from three SAMs in the industrial area. The VOCs emitted from the nearby factories are carried to point III by the southwestern or southern wind. The high terrain to the north of point III suppresses the long-distance transmission of VOCs, particularly the emission from nearby restaurants at night. Point IV is also close to the industrial districts, where VOC emissions during production and transportation result in significant response values, especially during working days. Furthermore, the flat terrain around

point IV facilitates the diffusion of VOCs. These points are mainly related to the activity of surrounding industries or the operation of heavy diesel trucks. Although the highest concentration can reach up to 700 ppb, the impact on the surrounding area is limited. There was no long-distance transmission and no high-concentration emission in the residential area.

To prove the effectiveness of the SAMs' network, vehicle-mounted GC-MS was further applied as a supplementary approach for monitoring TVOCs to provide more detailed component information. As shown in **Fig. 3**, the observations of high concentration positions (points I &VI) by vehicle-mounted GC-MS and SAMs' network (30th August, Monday) are similar (21 sets of the 33 SAMs that overlapped the course of the vehicle are consistent with a vehicle-mounted GC-MS with a MAPE within ±50%). The highest concentration of these two potential sources represents typical industrial characterization, with Hexene/Methylcyclopentane accounting for the vast majority (85.3% and 55.9%), followed by Butene (7.5% and 16.3%), according to the storage tanks of a 50 kT/a industrial 1-Hexene plant. Three points (points III, V and VII) are affected by both natural and traffic sources, where Isoprene (14.2%, 8.9% and 8.9%) and Pentene (14.6%, 12.8% and 8.2%) are identified as the significant contributors. Another two points (points II & IV) are contributed by industry/traffic, in which the predominant VOC components are Pentene (17.4%) and Hexene/Methylcyclopentane (13.3%). Although the SAMs' network and GC-MS measurements are comparable in high concentration areas, it should be noted that their observations are not equivalent due to different technologies, meteorological conditions and spatiotemporal distributions.

3.4 Site-specific abatement

The SAMs' network observed the obvious reduction of TVOC concentration over the course of 153 days. China has been striving to meet the climate commitments under the Paris Agreement (Rogelj et al., 2016). Peak carbon dioxide emissions and carbon neutrality were proposed in 2021 (Liu et al., 2021; Shi et al., 2021). A number of measures have been implemented in the factories to reduce emissions, including safety risk assessments of storage tanks, checking the leakage points of 1-hexene plant, and establishing daily monitoring reports of the ethylene plant. With the help of the SAMs' network, the impact of emission reduction measures implemented by the government and enterprises can be directly feedbacked. As a result, SAMs observe the obvious monthly decline in concentration (**Fig. 4a-f, Fig. S8**). Specifically, four high concentration points occurred

in August and September, which were located in a factory (I) and along the factory boundary with a highway (II, IV, and VI) were nearly vanished in December and January due to the strict abatement efforts. In contrast, there was just one high-concentration point in December and January, which was likely caused by highway traffic. In addition, emissions from natural sources have also been reduced over time as the seasons changed. The overall monthly TVOC concentration shows a downward trend due to the strict abatement efforts, the widespread use of new energy vehicles, climate change, and production activities impacted by the 2022 Beijing Winter Olympics (**Fig. 4g**).

The overall hourly and daily concentration trend was also analysed by categories during the abatement period. As shown in **Fig. 4h**, the average TVOC concentration of most installed SAMs fluctuates between 50 and 300 ppb during the operating period, which is consistent with the previously documented TVOC concentration in Beijing (Ting et al., 2008; Wei et al., 2014). The hourly and daily TVOC concentrations both follow the order: Factory > Factory boundary & highway > Highway > Factory boundary & pathway ≈ Residential area & pathway > Upwind. The lowest hourly-average concentration is at 13:00~16:00; nevertheless, the highest concentration is at 6:00~8:00 or 17:00~18:00. The higher daily-average concentration (**Fig. 4i**) is from Thursday to Sunday, while the lower concentration occurs from Monday to Wednesday. Such trends in an industrial area and highway may be attributed to industrial and artificial activities, such as emissions from heavy trucks driving through the factories and highways of factory boundaries.

4. Conclusions and Implications

Although many countries and regions have set targets to reduce greenhouse gas emissions by 2030 and 2050, long-term strategies need to be planned in advance and implemented at the regional level in order to completely reduce greenhouse gas emissions by the middle and end of this century. The key to developing the pollution control strategy is to identify the main sources (Huang et al., 2014). The high-resolution SAMs' network can accurately characterise the temporal and spatial variability of local air pollution, which is not available from superstations or other low spatial density instruments. For instance, we have observed that the concentration of two SAMs located just a few hundred metres apart can be over 100% deviation from each other, especially when the concentration is influenced by meteorological conditions and geographical

location (Liu et al., 2012). Therefore, a monitor close to the pollution source is necessary to effectively evaluate its impact on local air quality.

In this study, we unprecedentedly proposed low-cost SAMs and employed them to build a ~55-km^2 high-resolution TVOC network in southwest Beijing. To the best of our knowledge, this is the first-time electrochemical gas sensor arrays with machine-learning assistance have been proposed and applied for monitoring regional TVOCs. The source of pollution and its diffusion trend can be accurately and visually described based on spatial concentration information from the SAMs' network and component information from GC-MS. The large-scale, low-cost and high-resolution SAMs' network can bridge the gap between analysing equipment and prediction models. Considering that prediction models are usually speculated by extending data from a small number of devices or sparse networks to regional simulations, which, however, cannot accurately predict abrupt typical pollution sources. The construction and layout of the high-resolution SAMs' network can not only achieve accurate monitoring for the atmospheric station, but also eliminate numerous blind spots of environmental monitoring. The network provides an important basis for verifying environmental management efficacy, disease burden caused by airborne pollutants and environmental enforcement.

Developing better sensor arrays maintain a fundamental issue due to the widely unknown complex components in the atmosphere. The sensor arrays in this study simply apply several different electrochemical sensors with a machine-learning algorithm to represent TVOC concentration. Although they agree well with GC-MS for typical pollution events, they are still far from genuine consistency, making it difficult to precisely recognize the unidentified gases at present. The next stage is to improve the selectivity and optimise the algorithms of the sensors to improve their component recognition capabilities, thus can better identify the source of the pollution. The monitors integrated with diverse low-cost sensor technologies are considered as the way of the future. To satisfy more distribution needs, the development of monitors with low cost and low energy consumption via advanced nanomaterial and semiconductor technology, sustainable green energy technology and a smarter algorithm is also required.

In closing, policy plays a significant role in the network establishment and abatement of TVOCs. For instance, China has achieved great success in controlling PM$_{2.5}$ levels through policy guidance. In terms of carbon neutrality, many governments have also demonstrated their ambition. With the support of the SAMs' network, the efforts of the government and enterprises

are both considerable. Therefore, it is essential for the government to provide policy incentives and develop appropriate abatement measures.

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**Figures and captions**
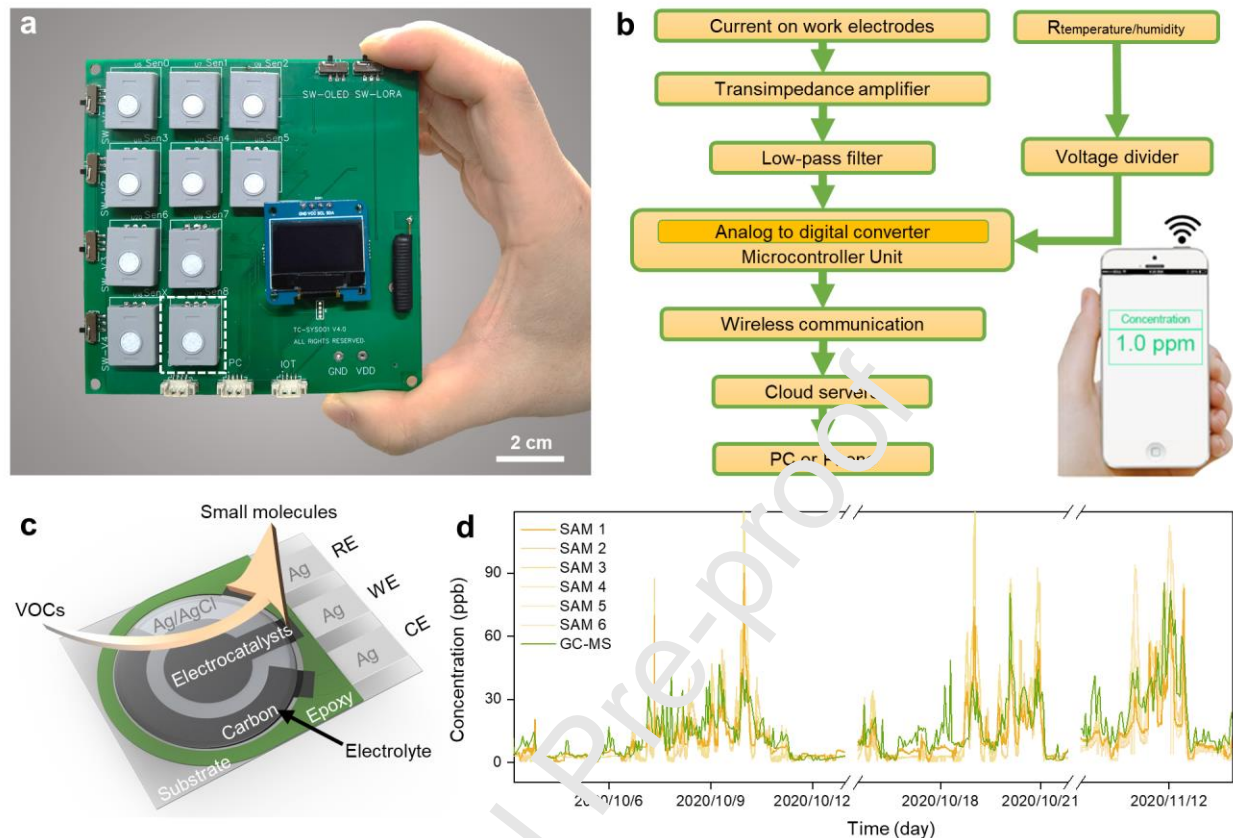
Fig. 1. **The reliable SAMs for monitoring TVOCs. a**, A photographic image of the sensor array and main integrated circuit of SAM. **b**, The system workflow of the SAM, including signal amplification, processing and transmission. **c**, Schematic illustration of the sensors on a SAM (RE, reference electrode; WE, working electrode; CE, counter electrodes). **d**, TVOC concentration in real atmospheric environment tested by SAMs and GC-MS (from 3 October to 13 November 2020).
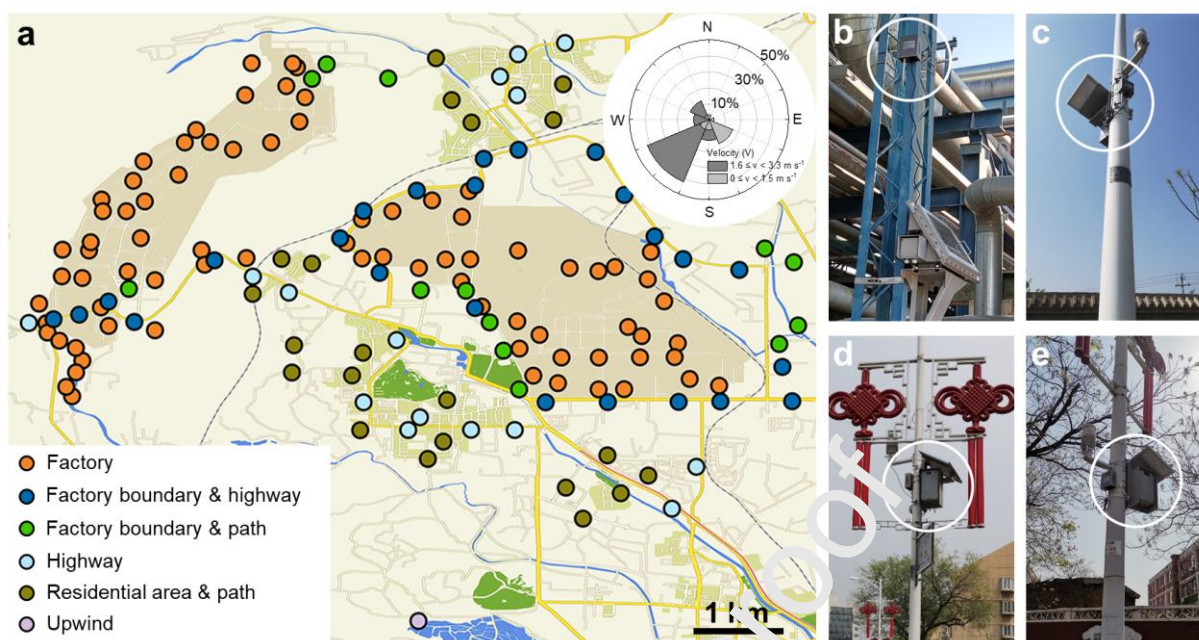
Fig. 2. **Deployment of a 152 sets of SAMs' network over a ~55-km^2 scale. a**, Installed SAMs assigned to six categories of location: (1) Factory (2) Factory boundary & highway, (3) Factory boundary & path, (4) Highway, (5) Residential area & path, (6) Upwind. **b-e,** Pictures of SAMs deployed over the ~55-km^2 area.
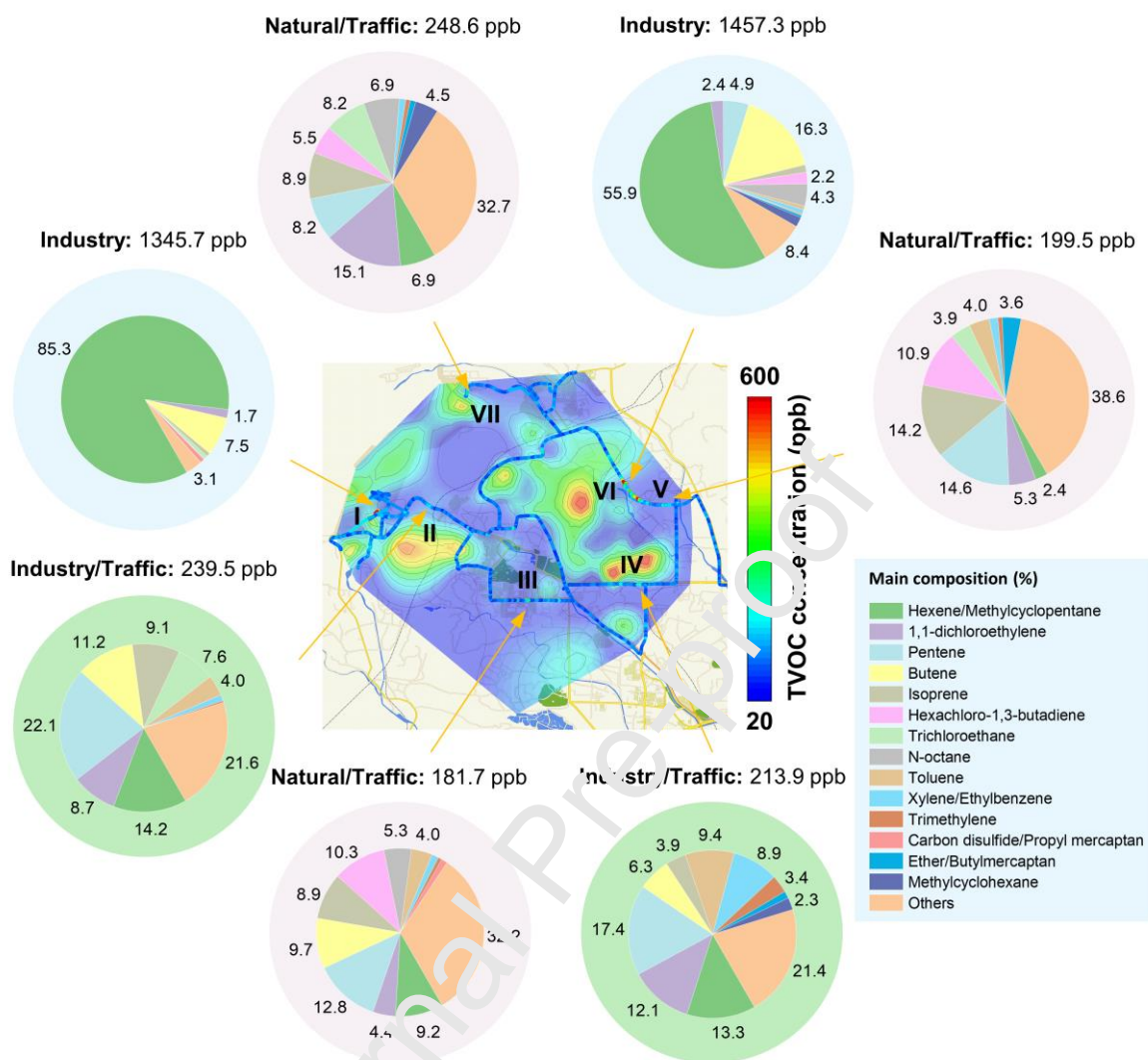
Fig. 3. Chemical composition and source apportionment of TVOCs on the afternoon of 30 August 2021 via joint observation of SAMs' network and vehicle-mounted GC-MS. The center is the TVOC concentration distribution map over the ~55-km² area, the stacked color lines are concentration tested by vehicle-mounted GC-MS, seven pie charts show TVOC composition at high-value areas tested by mass spectrometry.
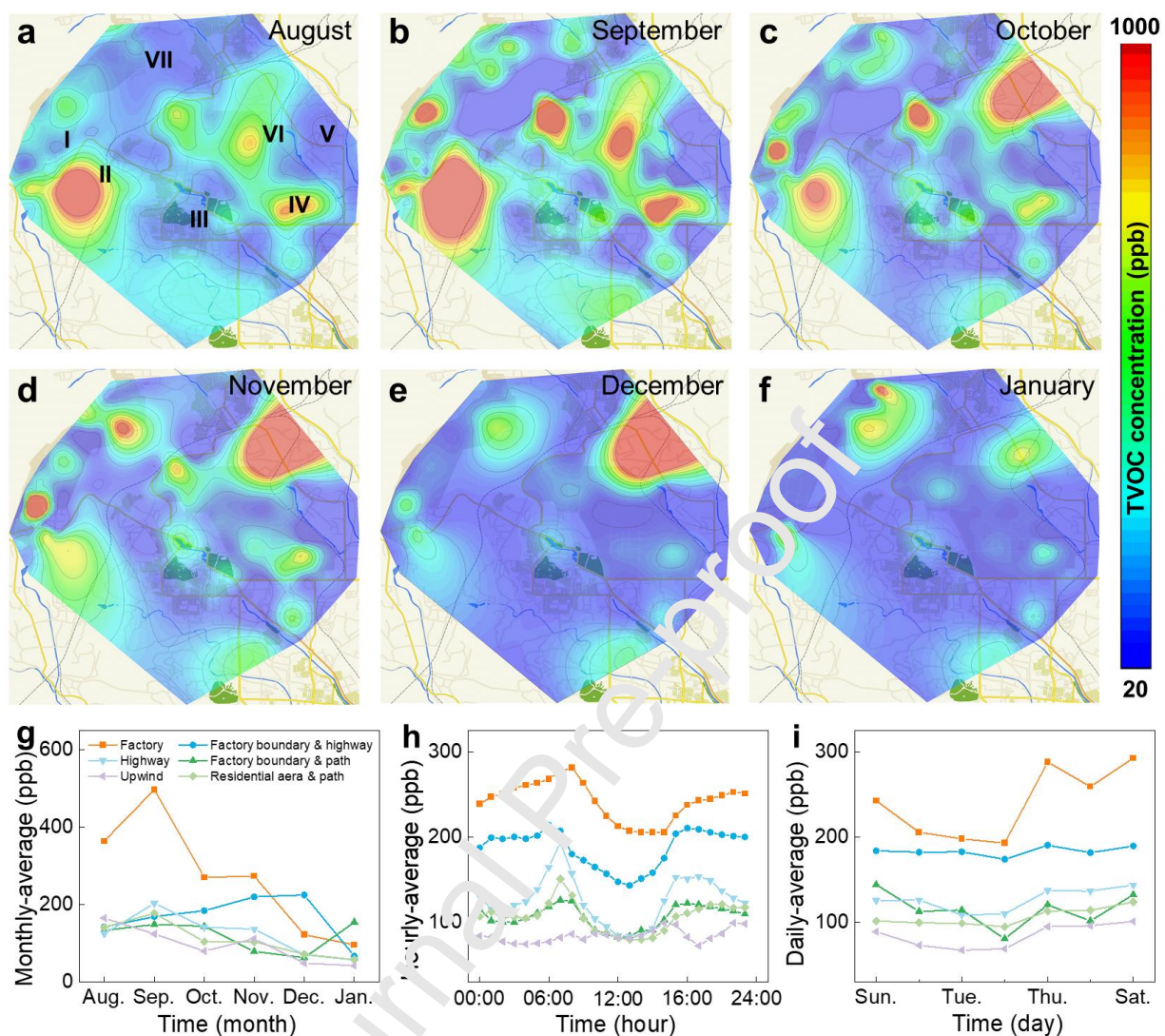
Fig. 4. TVOC concentration change trends from August 2021 to January 2022. a-f, Monthly-average TVOC concentration distribution maps over the location from August 2021 to January 2022. **g-i,** Monthly average, hourly average amd daily average TVOC concentrations of different categories over the ~55-km^2 area.

Author contributions

Zehui Li, and Yinglei Zhang conceived the project. Lingling Zhang, Diwei Zhu, Hui Li, Ziyi Wang, Pingchuan Xu and Yuexin Xu performed the sensors testing and installation experiments. Zizhen Ma, Zhan Zhang, Enze Tian, Haiteng Zhang, Ruiyao Yang, Minjung Kim, Yi Yuan and Xiaohui Qiao contributed the data analysis and processing. Dongbin Wang, Gang Wang, Mingjie Li, Yangyang Xie and Shaojun Guo contributed the writing and conception of the article. Important contributions to the interpretation of the results and conception were made by Zehui Li, Kaihui Liu and Jingkun Jiang. All the authors discussed the results and wrote the manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
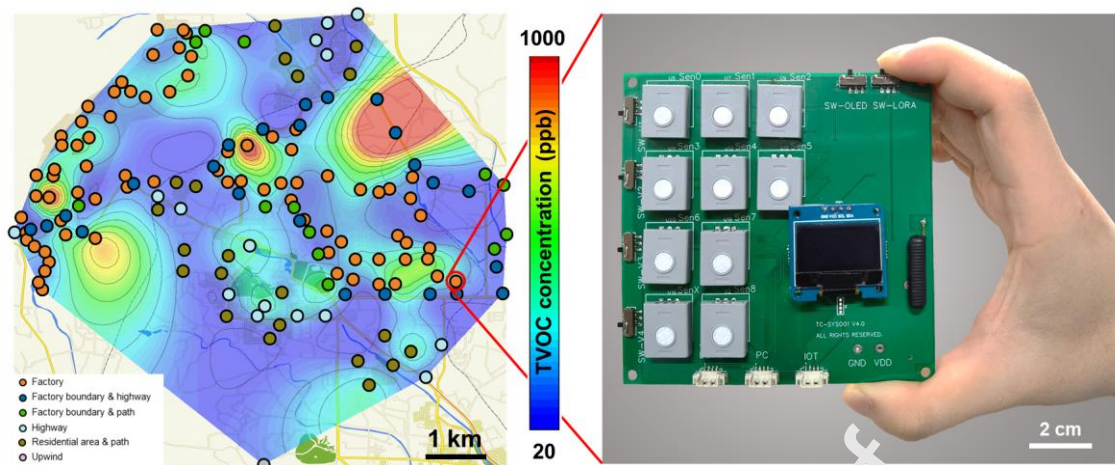
Graphical abstract

Highlights

- A sensitive and reliable sensor array is developed for VOC detection.

- A monitor based on the sensor array shows the consistent response with gas chromatography-mass spectrometry in the actual air environment.

- A low-cost and high-resolution VOC network of 152 sets of monitors across ~55 km^2 of mixed-used land is established.

- VOC network helps to reveal the polluted sources and effectively site-specific abatement.