

## Semi-volatile organic compounds in a museum in China: A non-targeted screening approach

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Non-targeted analysis (NTA) was conducted to identify semi-volatile organic compounds (SVOCs) in a museum in China using the gas chromatography (GC)-Orbitrap-mass spectrometer (MS). Approximately 160 SVOCs were detected, of which 93 had not been reported in previous studies of museum environments. Many of the detected SVOCs were found to be associated with the chemical agents applied in conservation treatment and the materials used in furnishings. The results of hierarchical cluster analysis (HCA) indicated a spatial variation of SVOCs in the indoor air in the museum, but there were no obvious temporal differences of SVOCs observed in indoor dust. Spearman's correlation analysis showed that several classes of SVOCs were well correlated, suggesting their common sources. Fragrances and plasticizers were found to be the primary sources of SVOC pollution detected in the museum. Compared with compounds in outdoor air, indoor SVOCs had a lower level of unsaturation and more portions of chemically reduced compounds. This study is the first of its kind to comprehensively characterize SVOCs in a museum using an automated NTA approach with GC-Orbitrap-MS. The SVOCs identified in the current study are likely to be present in other similar museums; therefore, further examination of their potential impacts on cultural heritage artifacts, museum personnel, and visitors may be warranted.

**non-target analysis, high-resolution mass spectrometry, semi-volatile organic compounds, museum environment, air pollutants**

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### 1 Introduction

For ages, museums have been used to preserve and exhibit a wide variety of cultural heritage artifacts. The protection and conservation of artifacts are highly related to the environmental conditions in museums, such as ventilation, temperature, humidity, light, and pollution [1]. Negative

conditions will accelerate the degradation of the collections and cause irreparable damage to them [2]. After long-term exposures to improper conditions, cultural heritages will undergo significant changes, and their lifetimes will be shortened due to the gradually accumulated environmental impact [3–5]. Previous studies of environmental conditions in museums focused mainly on temperature, light, and water vapor. Given that many air pollutants can cause adverse effects on artifacts, the impact of indoor air pollution on cultural assets has attracted wide attention over the past few

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years, which is also important for a healthy indoor environment for museum personnel and visitors [6–9].

Several studies on indoor air pollutants in museums have analyzed particulate matter or inorganic pollutants that are generated outdoors and subsequently infiltrated indoors, such as nitrogen oxides, sulfur dioxide, hydrogen sulfide, and ozone [8,10–15]. However, various chemical agents, such as plasticizers, flame retardants, pesticides, preservatives, and cleaning agents, have been used in large quantities, and these chemical agents are the primary indoor sources of volatile organic compounds (VOCs) and semi-VOCs (SVOCs) in museum environments [16–20]. There are various organic pollutants in museums, and often they are abundant. They may directly cause damage to cultural relics through oxidation or hydrolysis [21], and further generate harmful byproducts when they interact with other environmental factors such as temperature, humidity, light, and mold. Many VOCs have been found to cause surface efflorescence on carbonate materials, fading and degradation of pigments, depolymerization of organic-based objects, and corrosion of metal [17,18,22–28].

In addition to VOCs, there are large numbers of SVOCs with more diverse properties and more complex sources in indoor environments [29]. However, only limited studies have reported the indoor air pollution of SVOCs in museums, and these studies focused mainly on pesticide residues, such as organochlorine pesticides (OCPs) [7,9,30,31]. Previous research in museums primarily conducted targeted analysis (TA) methods for the detection of organic compounds [16]. Although the TA methods have the advantages of high sensitivity and reproducibility, they only allow the detection of a limited number of preselected compounds, and they fail in detecting unknown or emerging chemicals. The indoor chemicals include a wide range of SVOCs with respect to molecular mass, functional group distribution, and polarity at trace levels, so the characterization of the overall SVOC composition in museums is challenging. However, it is necessary to obtain a better understanding of the potential risks that indoor air poses to their collections and their potential cumulative exposures and impacts on museum personnel and visitors.

In recent years, the application of high-resolution mass spectrometry (HRMS) coupled to gas chromatography (GC) or liquid chromatography (LC) for non-targeted analysis (NTA) has developed rapidly [32]. HRMS instruments, most notably orbitrap and quadrupole time-of-flight (Q-TOF), provide high mass accuracy and resolving power to facilitate chemical identification in complex matrices [33–36]. With these enhancements, NTA has initiated new possibilities for detecting and elucidating unknown or emerging contaminants from multiple compound classes without the preselection of analytes [37–39]. While significant progress has been made for the non-targeted screening of unknown con-

taminants in various environmental compartments, such as water, soil, aerosols, and sediments [33–35,40–43], research on organic compounds, especially SVOCs in indoor environments, is still limited. Only a few studies have applied NTA methods to identify SVOCs in household dust [44–47].

This study is part of a research project that is focused on indoor pollutants in museums. The objectives of this study are (1) to apply an automatic NTA screening approach to identify the tentative composition and distribution of SVOC pollutants in indoor air and dust samples collected from a museum in Beijing; (2) to investigate the relationship among indoor SVOCs and their potential emission sources in the museum; (3) to compare the molecular nature of the SVOC compounds in the museum with those in outdoor air. To the authors' knowledge, this study is the first of its kind to apply the NTA screening approach using the GC-Orbitrap-MS to characterize indoor SVOCs in museum environments. It allows scientists and conservators to make direct use of the results to prioritize SVOC contaminants that may have impacts on cultural heritage artifacts, museum personnel, and visitors.

## 2 Materials and methods

### 2.1 Chemicals

Dichloromethane (DCM) and hexane (ultrapure, spectroscopy grade, >99.9%) were supplied by Merck (Germany). Phenanthrene, anthracene, 2-phenoxyethanol, 2,4-di-*tert*-butylphenol, 2-methylnaphthalene, pyrene, dibutyl phthalate, diisobutyl phthalate, chloroxyleneol, 2-ethylhexanoic acid, galaxolide, heptadecane-1-ol, dimethyl phthalate, dibenzofuran, 1,6,7-trimethylnaphthalene, biphenyl, 4-*tert*-butylphenol, 2-vinylnaphthalene, diphenylacetylene, 1-pentadecanol, C<sub>8</sub>–C<sub>40</sub> alkanes and 1,4-dichlorobenzene-d<sub>4</sub> standard solutions (purity >98%, concentration ranging between 100 and 1000 µg/mL) were purchased from Accustandards Inc. (USA).

### 2.2 Sampling site

The museum in which the samples were obtained is located in the center of Beijing. It covers a land area of 70000 m<sup>2</sup>, and it houses more than a million items, including ancient and modern artifacts, rare and antiquarian books, and works of art. The heating, ventilation, and air conditioning (HVAC) system is operated throughout the entire building. The temperature, relative humidity, and air change rate are strictly controlled at 20°C±2°C, 45%±5%, and 1±0.1 h<sup>-1</sup>, respectively. Figure 1 shows the different sampling sites selected in an exhibition hall (800 m<sup>2</sup>), including air sampling sites and dust sampling sites, in which a temporary exhibition of selected artifacts made of ceramics, metal, paper, textiles, and wood products was held.



**Figure 1** (Color online) Schematic diagram of the air and dust sampling sites in the museum. Sampling sites 1 to 4 were corresponding to air samples I to IV.

### 2.3 Sample collection and preparation

In order to reflect the long-term indoor air pollution in the exhibition hall, passive sampling was conducted to collect air samples, which has the advantages of long sampling time, low noise, no power requirements, and convenient operation. Polyurethane foam (PUF) disks ( $\sim 80 \text{ cm}^2$ , TE-1014, TISCH Environmental, USA) were used for passive air sampling. Prior to use, the disks were cleaned with DCM and conditioned in an oven at  $80^\circ\text{C}$  for 30 min to remove any contaminants. Then, each disk was inserted into the center hole of a stainless-steel holder, and the assembly was installed in a passive sampler. Triplicate passive samplers were placed at each sampling location for approximately three weeks in December 2019. In addition, dust sampling was conducted using a modified vacuum cleaner that contained a cellulose extraction thimble (7100-3080, Ahlstrom-Munksjö, Sweden) like those that commonly are used to sample indoor dust. During sampling, the vacuum cleaner was held and moved slowly over the floor of the exhibition hall to collect dust samples in the area marked in Figure 1. After dust sampling, the extraction thimbles were sealed immediately with aluminum foil to avoid contamination. Two sampling events were conducted in December 2019, and there was an interval of one week between the two events. When the sampling was completed, the passive samplers and extraction thimbles were wrapped with aluminum foil, sealed in a zip bag, stored in a freezer at a temperature of  $-80^\circ\text{C}$ , and analyzed within two days of sampling.

The samples collected by different samplers were prepared using the solvent extraction method. Each PUF disk and each extraction thimble were ultrasonically extracted three times

with 10 mL of hexane/DCM (1:1, v:v) for 15 min each time. A Branson M5800 ultrasonic cleaner filled with clean water was used for the extractions. Ice bags were used to maintain a low water temperature to avoid the loss of target chemicals by evaporation during ultrasonication. After cleaning with preassembled filtration devices (Whatman Autovial<sup>TM</sup> syringeless PTFE filters with  $0.2 \mu\text{m}$  pore), the extract was concentrated to approximately 1 mL using an evaporator (Buchi, SyncorePlus Analyst) followed by gentle purging with a high-purity nitrogen stream.

### 2.4 Chemical analysis with HRMS

A Trace 1310 GC coupled with a Q Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, USA) was used for GC NTA. GC separation was performed on a  $30 \text{ m} \times 0.25 \text{ mm}$ ,  $0.25 \mu\text{m}$  DB-5MS column (Agilent, USA) with carrier gas flow (helium) at 1.2 mL/min. The GC oven temperature program started at  $50^\circ\text{C}$ , and held for 3 min, followed by a ramp at  $25^\circ\text{C}/\text{min}$  to  $180^\circ\text{C}$ , a second ramp at  $5^\circ\text{C}/\text{min}$  to  $320^\circ\text{C}$ , held for 5 min. The hot splitless injection was carried out at  $280^\circ\text{C}$  and the volume of the injection was 1  $\mu\text{L}$ .

MS was operated in a scan mode using an  $m/z$  range of 60–900 with a resolution of 60000 in electron ionization (EI). The detailed MS parameters were ion source temperature:  $280^\circ\text{C}$ ; ion source voltage: 70 eV; transmission line temperature:  $250^\circ\text{C}$ ; the filament delay: 3 min. During the analysis, internal mass calibration was performed by the instrument using three background ions that originated from the column bleed as lock mass ( $\text{C}_5\text{H}_{15}\text{O}_3\text{Si}^{3+}$ , 207.03236;  $\text{C}_7\text{H}_{21}\text{O}_4\text{Si}^{4+}$ , 281.05115;  $\text{C}_9\text{H}_{27}\text{O}_5\text{Si}^{5+}$ , 355.06994) with a

search window of  $\pm 2$  ppm. Before and after the sample sequence, a mixture of C<sub>8</sub>–C<sub>40</sub> saturated *n*-alkanes standard (Sigma-Aldrich Co. LLC.) was run to calculate the retention time index (RI) of all non-targeted candidates. The deviation of the retention time (RT) of *n*-alkanes before and after the sample sequence should be less than  $\pm 1\%$ . At least five points (ranging from 1 ng/mL to 1  $\mu$ g/mL) were included in each calibration line. All standards for calibration were prepared in hexane.

## 2.5 HRMS data processing

The data processing method followed our previously developed NTA workflow [48]. Briefly, GC-HRMS raw data files were deconvoluted to extract individual peaks from the total ion chromatogram (TIC) using the deconvolution plug-in application for TraceFinder 5.1 software (Thermo Scientific, USA). Peak deconvolution was processed with all ions in the deconvoluted spectra for library search, an accurate mass tolerance (+/–) of 5 ppm, an S/N (signal to noise) threshold of 3, a minimum TIC intensity threshold of  $9 \times 10^4$ , and an ion overlap window of 98%. RT of *n*-alkanes was input in RI *n*-alkane list to calculate the experimental RI. Tentative identification was done by comparing the nominal National Institute of Standards and Technology (NIST) 2017 main mass spectral library with the component spectrum for each peak extracted by peak deconvolution. Tentative candidates for each peak were scored based on a classical search index (SI) score and a high-resolution filtering (HRF) score. All candidates were filtered based on a minimum setting value of 7 min of RT, a 700 SI score, and a 90 HRF score. After filtering, the list of tentative candidates for each peak was exported from TraceFinder for further analysis.

A one-stop, open-source R script was programmed to perform RI analysis. The simplified molecular input line entry system (SMILES) string of each candidate was searched from the PubChem database [49]. In the next step, RI values on the semi-standard non-polar stationary phase were predicted based on SMILES strings by the DeepRel in-silico software package [50]. The SMILES string and DeepRel RI of each candidate were input into a local database after the in-silico prediction. For further analysis, if the SMILES string of a candidate is already in the local database, the DeepRel RI can be searched directly from the database to skip the in-silico prediction step.  $\Delta$ RI (%) of each candidate was defined as the relative error between the experimental RI and the DeepRel RI. The levels of confidence for the identification of detected compounds were classified according to Song et al. [48].

## 2.6 Data analysis

Hierarchical clustering analysis (HCA) was performed

without a priori grouping information to examine the similarity and variation of field samples. The hierarchical agglomerative clustering using Ward's method was performed, in which the similarity between two objects is calculated using the maximum distance to assess which samples were similar and organized them into an ordered grouping, referred to as a hierarchical tree or dendrogram [51]. A Shapiro-Wilk test of normality indicated that the abundances of identified compounds were not normally distributed. Therefore, Spearman's rank-order correlation analysis, which is a nonparametric method that has been widely used [52,53], was performed to investigate the relationships between the detected compounds. To reduce the number of false positives for multiple comparisons, the Bonferroni correction to the significance level ( $\alpha$ ) was applied to Spearman's rank-order correlation analysis.

Indoor air pollutants may have adverse effects on the artifacts and the museum environment. Therefore, several metrics were used to describe the chemical characteristics of SVOCs in indoor air [16]. The extent of unsaturation of a molecule was characterized by the double-bond equivalent (DBE) that represents the number of double bonds and ring structures in the molecule. It can be expressed as

$$\text{DBE} = 1 + \frac{1}{2}(2C - H - X + N + P), \quad (1)$$

where *C*, *H*, *X*, *N*, and *P* respectively represent the number of the carbon, hydrogen, halogen, nitrogen, and phosphorus atoms in the compound. However, since DBE may not accurately characterize the unsaturation properties of compounds with heteroatoms (e.g., O, N, and S), the aromaticity equivalent (*X<sub>C</sub>*) was also calculated using the following equation:

$$X_C = \frac{3[\text{DBE} - (mO + nS)] - 2}{\text{DBE} - (mO + nS)}, \quad (2)$$

where *O* and *S* represent the number of oxygen and sulfur atoms, respectively; *m* and *n* represent the fraction of oxygen and sulfur atoms in the  $\pi$ -bond structure in the compound. In the current study, we used *m* = *n* = 1 for the conservative calculation of the *X<sub>C</sub>*, assuming that every oxygen and sulfur atom was considered as a  $\pi$ -bond structure [54]. If  $\text{DBE} \leq mO + nS$  or  $X_C \leq 0$ , then *X<sub>C</sub>* was defined as zero. Threshold values for *X<sub>C</sub>* were proposed in the literature [54,55], where  $X_C \geq 2.5$  and  $X_C \geq 2.7$  are the minimum criteria for the presence of aromatic and condensed aromatic structures, respectively. The oxidation state of the carbon atoms (*OS<sub>C</sub>*) in the organic compounds was calculated using eq. (3), according to Kroll et al. [56]:

$$\text{OSC} \approx 2O/C - H/C, \quad (3)$$

where *O/C* and *H/C* are the molar ratios of oxygen and hydrogen to carbon, respectively. These calculations provided a convenient and effective method for comparing the structural characteristics of different SVOCs. The average values of the



DBE,  $X_C$ , and  $OS_C$  for indoor and outdoor air pollutants were calculated to provide a visual representation of the overall chemical characteristics of the pollutants.

## 2.7 Quality assurance and quality control

Triplicate samples were collected at all sampling sites during each sampling event. The discrepancy of chemical species between duplicate samples was less than 15%. Field and laboratory blanks were analyzed along with the samples using the same pretreatment and chemical analysis methods, and the features detected in the blanks were subtracted automatically by the TraceFinder software during data analysis to avoid the impact of background contamination. Hexane blanks were run intermittently to reduce potential carryover and served as solvent blanks. An internal standard was spiked into each sample to normalize each run and estimate the tolerance of mass accuracy and RT drift. An isotopically-labeled chemical standard, 1,4-dichlorobenzene- $d_4$ , was spiked to the sample as a surrogate to check the recoveries of compounds during extraction. Solvent blanks were analyzed at the beginning and end of the sample sequence, and before and after quality control samples to monitor carryover and memory effects. All chemical standards used in this study were of high purity (>98%). Periodic tuning and calibration of the HRMS instrument were performed every time before the sample batch run. Three characteristic ions ( $C_5H_{15}O_3Si^{3+}$ , 207.03236;  $C_7H_{21}O_4Si^{4+}$ , 281.05115;  $C_9H_{27}O_5Si^{5+}$ , 355.06994) were monitored for internal mass calibration.

## 3 Results and discussion

### 3.1 Non-targeted screening of SVOCs

The deconvolution of the GC-Orbitrap-MS chromatograms covered over ten thousand features in all samples. After automatic data processing, 158 SVOCs were tentatively identified with confidence level 3 or above. A SciFinder search was conducted by querying the term “museum” or “indoor environment”, and the CAS number of each chemical to determine whether the chemicals tentatively identified via NTA in this study had been measured previously in museum or indoor environments [47]. Of the 158 compounds, 93 have not been reported in previous studies in the museum environment, and 34 of them have not been detected in the indoor environment. The literature investigation suggested that NTA was valuable in characterizing contaminants in the indoor environment.

As shown in Figure 2, HCA was performed without a priori grouping information to examine the similarity and variation of field samples. The peak abundance of SVOCs was used to represent SVOC concentrations. The detected SVOCs were classified into 10 categories, i.e., heteroatoms, esters, al-

kanes/-enes/-ynes, naphthalenes, arenes, alcohols, ethers, aldehydes, acids, and ketones. Among them, naphthalenes, arenes, aldehydes, heteroatoms, and ethers were detected mainly in air samples, while ketones were more abundant in dust samples. This was probably due to the different partition coefficients of SVOCs between air and dust. According to the results of the HCA, two distinct clusters were separated by air and dust samples, suggesting the different SVOC compositions in air and dust in museum environments. Air samples at Site 1 and Site 2 were gathered, and Site 3 and Site 4 were gathered. The results indicated the variety of chemical species and their air concentrations at different sampling sites in the museum. Two dust samples collected in the same area one week apart had very similar chemical compositions. Therefore, significant spatial variations of indoor gaseous SVOCs in the museum were observed during sampling, but there were no obvious temporal changes of the SVOCs in the dust samples.

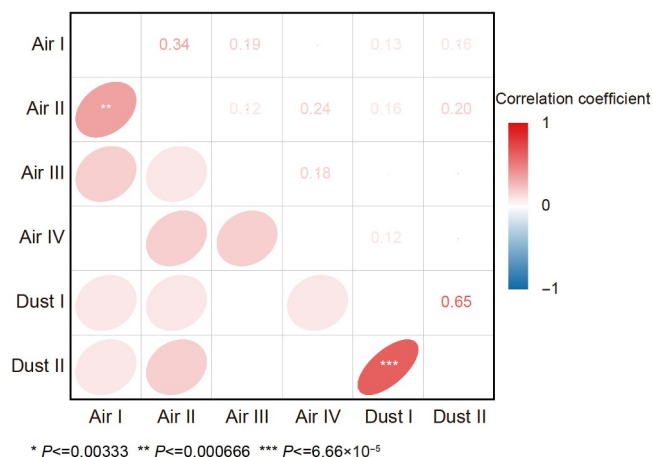
### 3.2 Correlation analysis

Spearman's correlation analysis was performed using R (v3.4.4) for all samples in order to evaluate the relationships between them, as shown in Figure 3. The Shapiro-Wilk test indicated that the data did not conform to a normal distribution before or after logarithmic correction. Therefore, the Spearman correlation test was utilized. After a strict Bonferroni correction for  $p$ -values, a strong significant correlation was observed between Dust I and Dust II, and a weak significant correlation was observed between Air I and Air II. The results matched well with the HCA. The strong correlation between Dust A and Dust B indicated that the composition of SVOCs in dust was similar during different sampling events, which was similar to the results of previous studies [57]. However, several studies pointed out that the SVOC composition in indoor dust could change with the seasons, which was caused primarily by the change of indoor SVOC sources in different months, especially for various consumer products used in different seasons [57,58]. Since there was only one month between the two sampling events in our study, the chemical compositions of the two dust samples may not be very different due to the similar chemical sources in the museum. The significant correlation between Air I and Air II indicated a high overlap between the SVOC compositions at the two sampling sites that were close to each other, as shown in Figure 1.

For specific SVOCs, their correlations in air and dust samples were also investigated. Figure 4 indicates that there were significant correlations ( $r \geq 0.82$ ,  $P < 0.006$ ) among benzenes, naphthalenes and phthalates, including biphenyl, dibenzofuran, 2-ethenylnaphthalene, methylnaphthalene, 2-methylnaphthalene, and dimethyl phthalate. The co-occurrence of a number of arenes and naphthalenes was also



**Figure 2** Heatmap of HCA of 158 detected SVOCs at confidence level 3 or above. The color intensity represents the average abundance of detected compounds in each kind of sample. The column on the right represents the chemical classes. Chemical CAS numbers are listed on the left.



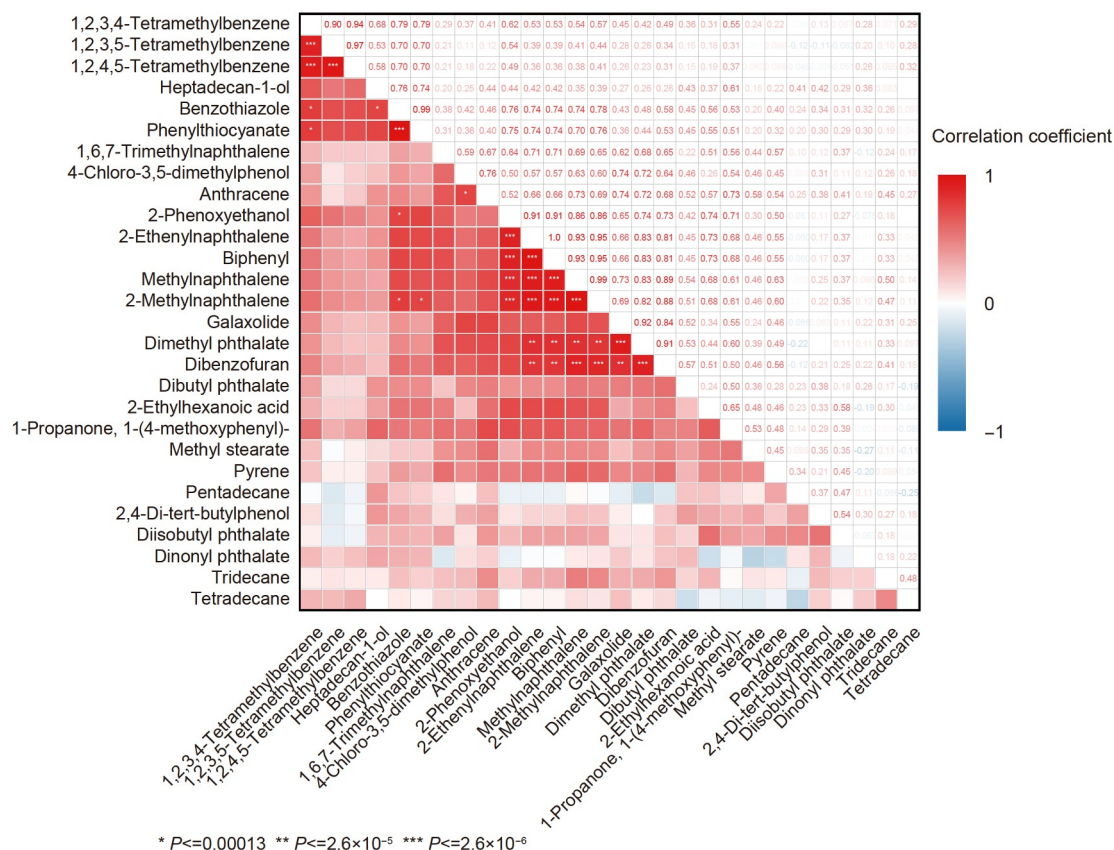
**Figure 3** Results of the Spearman correlation analysis between different kinds of air and dust samples in the exhibition hall. The \* symbols represent significant levels, and the  $P$ -values are Bonferroni-corrected.

observed in several museums in Spain [59]. Besides, benzothiazole and 2-phenoxyethanol had a strong correlation ( $r = 0.76$ ,  $P = 0.042$ ). The co-occurrence of benzothiazole and 2-phenoxyethanol was also observed in a previous indoor environmental study [60]. 2-Methylnaphthalene presented a strong correlation with both benzothiazole and 2-

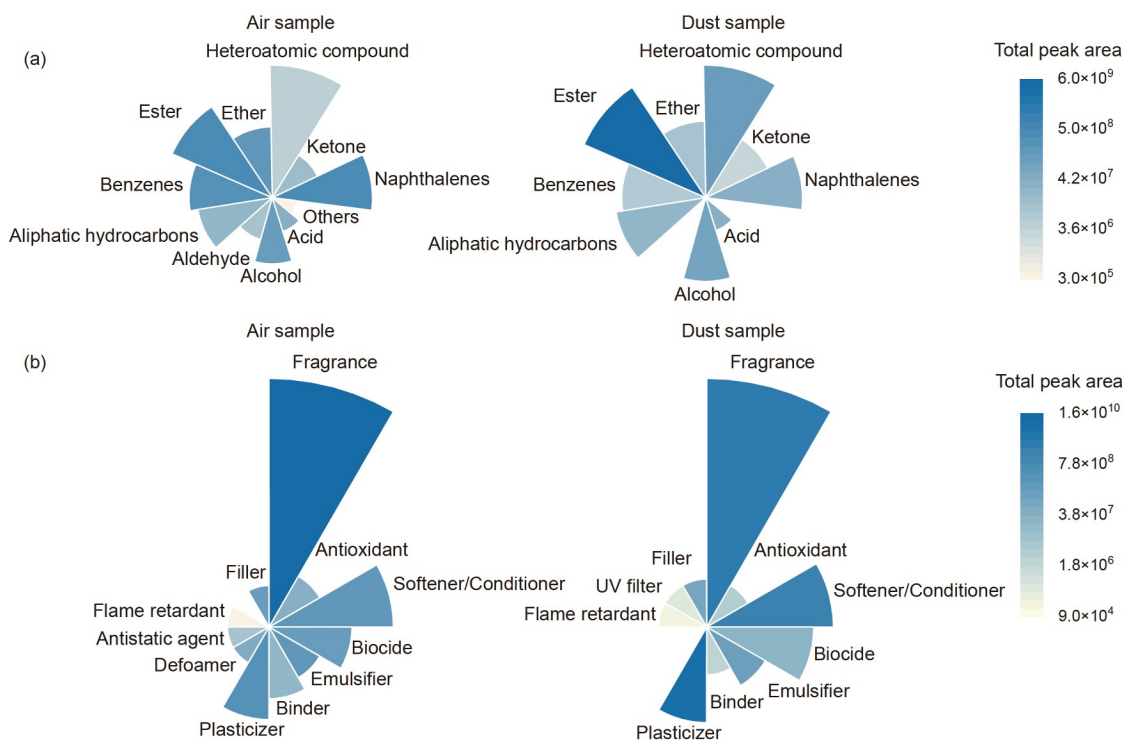
phenoxyethanol ( $r \geq 0.76$ ,  $P < 3.6 \times 10^{-4}$ ). These chemicals are all products of the combustion of petroleum, which may come from the exhaust from cars in the outdoor air [61]. In addition, there were strong correlations among 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,4,5-tetramethylbenzene ( $r \geq 0.9$ ,  $P < 2 \times 10^{-5}$ ), and a strong correlation between benzothiazole and phenylthiocyanate ( $r = 0.99$ ,  $P = 2 \times 10^{-13}$ ). It revealed the co-occurrence of SVOC isomers in museum environments. The co-occurrence of 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,4,5-tetramethylbenzene may be related to their common usage as starting materials in the organic synthesis of plastics and resins [62].

### 3.3 SVOC composition

The distribution of chemical classes of detected SVOCs is depicted in Figure 5(a). The chemical concentrations were represented by their peak abundance. Esters and naphthalenes were the most abundant chemicals in the air samples, which had both high numbers of compounds and concentrations. Although the air samples contained the highest number of heteroatomic compounds, their total concentrations were very low. For the dust samples, esters and het-



**Figure 4** Correlation analysis among SVOCs with a confidence level of 3 or above and detection frequency higher than 50% in air or dust samples. The color mapping indicates the magnitude of the correlation coefficient, the \* symbols indicate significance levels, and the  $P$  values are Bonferroni-corrected.



**Figure 5** Distribution of (a) chemical class and (b) functional use of SVOCs detected with a confidence level of 3 or above in air and dust samples. Sector area indicates the detected number of the compounds, and color intensity indicates the total peak area of the compounds.

eroatomic compounds were the primary classes of SVOCs, with the highest numbers and the highest total concentrations of chemicals. Many naphthalenes were also contained in the dust samples, but their concentrations were much lower than the concentrations in the air samples due to their high vapor pressure. To further investigate the sources of SVOCs in the museum, we retrieved their functional uses from the Chemical and Products Database (CPDat), which contained nearly 150000 functional uses of over 10000 compounds [63]. The functional uses of 68 compounds were included in the database, and their distribution in the air and dust samples is shown in Figure 5(b). A total of 58 compounds were used as fragrances, including many esters, heteroatomic compounds, and naphthalenes, as shown in Table S1. Fragrances are widely used to control odors or to impart pleasing odors [64]. In museums, fragrances could also arise from cleaning products used routinely or from perfumes worn by museum visitors or staff [65,66]. These may lead to their extremely high concentrations in the air and dust samples. Several esters, such as dimethyl phthalate and diethyl phthalate, are also used extensively as plasticizers in building materials and exhibition facilities [18]. Therefore, the total concentration of plasticizers in the dust samples was also high. In addition, some identified compounds were also reported in the museum in previous studies. Alvarez-Martin classified methyl palmitate as a cosmetic or personal hygiene product in the museum environment [67]. Heptanoic acid was found to be

emitted from wood-based materials in the museum [68]. Oleyl alcohol was detected in fabric materials in the museum, which was potentially used as a surfactant [16,69].

A total of 17 Level 2 compounds were confirmed using chemical standards, and they were upgraded to Level 1 [48], as listed in Table 1. Among them, 2,4-di-*tert*-butylphenol, 2-methylnaphthalene, galaxolide, 4-*tert*-butylphenol, and 2-vinylnaphthalene have not been detected in museum environments, and 2-vinylnaphthalene has not been identified in indoor environments [70]. 2-Vinylnaphthalene is widely used as a chemical intermediate in many products, such as dyes, flame retardants, and plasticizers [71]. 2,4-Di-*tert*-butylphenol was identified as an antioxidant or a plasticizer in the plastic samples [72]. 2,4-Di-*tert*-butylphenol and 4-*tert*-butylphenol are both phenol derivatives. They may be used as anti-corrosive and anti-mold agents for paper artifacts [73]. However, due to their high corrosiveness, they can cause the deterioration of paper, thus reducing its durability and shortening its preservation time. 4-Chloro-3,5-dimethylphenol can be used as a preservative to protect pyritic specimens from *Thiobacilli* and *Ferrobacilli* in museum storage [74]. 2-Methylnaphthalene is a product of the combustion of petroleum, which may come from the exhaust of cars in the outdoor air [61]. Galaxolide is a synthetic musk that is commonly used as a fragrance for enhancing scent and covering odor [75]. The results strengthened the suitability of the NTA approaches for the screening of SVOCs in museums



**Table 1** List of confirmed SVOCs in museum environments

CAS number	Chemical name	Chemical formula	Chemical class	Molecular weight	Detection frequency <sup>a)</sup>	HPV <sup>b)</sup>	SciFinder hits (indoor) <sup>c)</sup>	SciFinder hits (museum) <sup>c)</sup>	Chemical usage <sup>d)</sup>
85-01-8	Phenanthrene	C <sub>14</sub> H <sub>10</sub>	Naphthalene	178.08	100%		498	2	N.A.
120-12-7	Anthracene	C <sub>14</sub> H <sub>10</sub>	Naphthalene	178.08	100%	✓	437	2	N.A.
122-99-6	2-Phenoxyethanol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	Ether	138.07	85%	✓	49	3	Antioxidant, biocide, foamant, fragrance, plasticizer, preservative, surfactant
96-76-4	2,4-Di- <i>tert</i> -butylphenol	C <sub>14</sub> H <sub>22</sub> O	Alcohol	206.17	90%	✓	13	0	N.A.
91-57-6	2-Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	Naphthalene	142.08	100%	✓	60	0	Fragrance
129-00-0	Pyrene	C <sub>16</sub> H <sub>10</sub>	Naphthalene	202.08	90%		530	3	N.A.
84-74-2	Dibutyl phthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	Ester	278.15	100%	✓	344	11	Fragrance, plasticizer
84-69-5	Diisobutyl phthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	Ester	278.15	100%	✓	188	1	N.A.
88-04-0	4-Chloro-3,5-dimethylphenol	C <sub>8</sub> H <sub>9</sub> ClO	Alcohol	156.03	80%		1	2	Biocide, fragrance, preservative
149-57-5	2-Ethylhexanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Acid	144.12	75%	✓	29	1	N.A.
1222-05-5	Galaxolide	C <sub>18</sub> H <sub>26</sub> O	Ether	258.20	85%	✓	53	0	Fragrance
131-11-3	Dimethyl phthalate	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	Ester	194.06	100%	✓	196	7	Fragrance
132-64-9	Dibenzofuran	C <sub>12</sub> H <sub>8</sub> O	Ether	168.06	95%		98	1	N.A.
2245-38-7	1,6,7-Trimethylnaphthalene	C <sub>13</sub> H <sub>14</sub>	Naphthalene	170.11	90%		9	1	N.A.
92-52-4	Biphenyl	C <sub>12</sub> H <sub>10</sub>	Benzenes	154.08	100%	✓	317	11	Fragrance
98-54-4	4- <i>Tert</i> -butylphenol	C <sub>10</sub> H <sub>14</sub> O	Alcohol	150.10	80%	✓	19	0	N.A.
827-54-3	2-Vinylnaphthalene	C <sub>12</sub> H <sub>10</sub>	Naphthalene	154.08	85%		0	0	N.A.

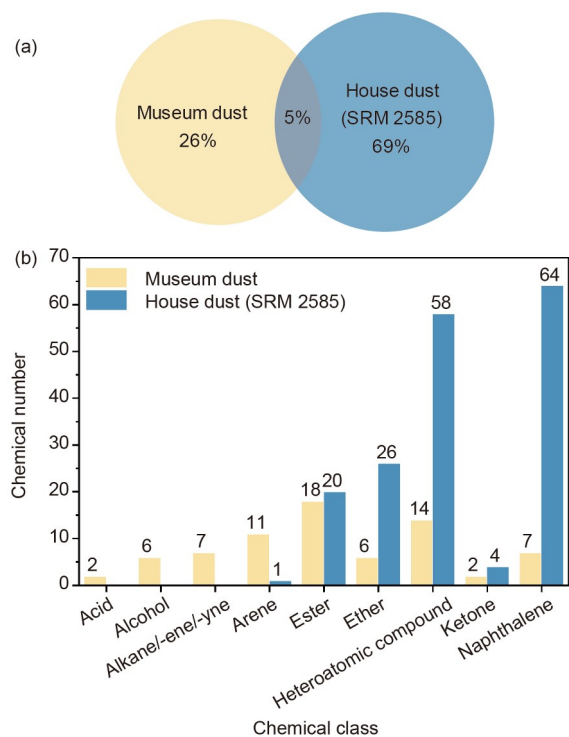
a) Detection frequency reflects the occurrence of the chemical confirmed in air and dust samples. b) High production volume (HPV) recorded by U.S. Environmental Protection Agency CompTox Chemicals Dashboard (<https://comptox.epa.gov/dashboard/chemical-lists/EPAHPV>). c) SciFinder hits reflect the number of journal references that resulted from querying SciFinder (Apr. 2022) for each CAS number and the term “indoor”/“museum” (<https://scifinder-n.cas.org/>). d) Chemical usage recorded by U.S. Environmental Protection Agency’s Chemical and Products Database (CPDat) (<https://www.epa.gov/chemical-research/chemical-and-products-database-cpdatt>).

and other indoor environments.

We compared the chemical compositions of the dust in the museum to the chemical compositions of house dust. Newton et al. [33] reported the compounds identified in Standard Reference Material (SRM) 2585 Organic Contaminants in House Dust, and 173 SVOCs were detected in SRM 2585, such as polycyclic aromatic hydrocarbons, phthalates, and OCPs, while 73 SVOCs were detected in the museum dust with a confidence level of 3 or above. Among them, 12 of the chemicals overlapped. The Venn diagram (Figure 6(a)) shows the percentage of SVOCs measured in museum and house dust. The number of SVOCs detected in each chemical class in the museum and house dust is shown in the histogram (Figure 6(b)). Naphthalenes were found to be used to control pests and to store the collections in museums [76,77]. However, the house dust may contain more kinds of naphthalenes, mainly due to the multiple sources in indoor environments, including smoking, cooking, heating, and household cleaning [78,79]. Besides, there were also more heteroatomic compounds and ethers found in house dust than in museum dust, indicating the distinct SVOC compositions in the museum and indoor environments.

### 3.4 Comparison with outdoor air

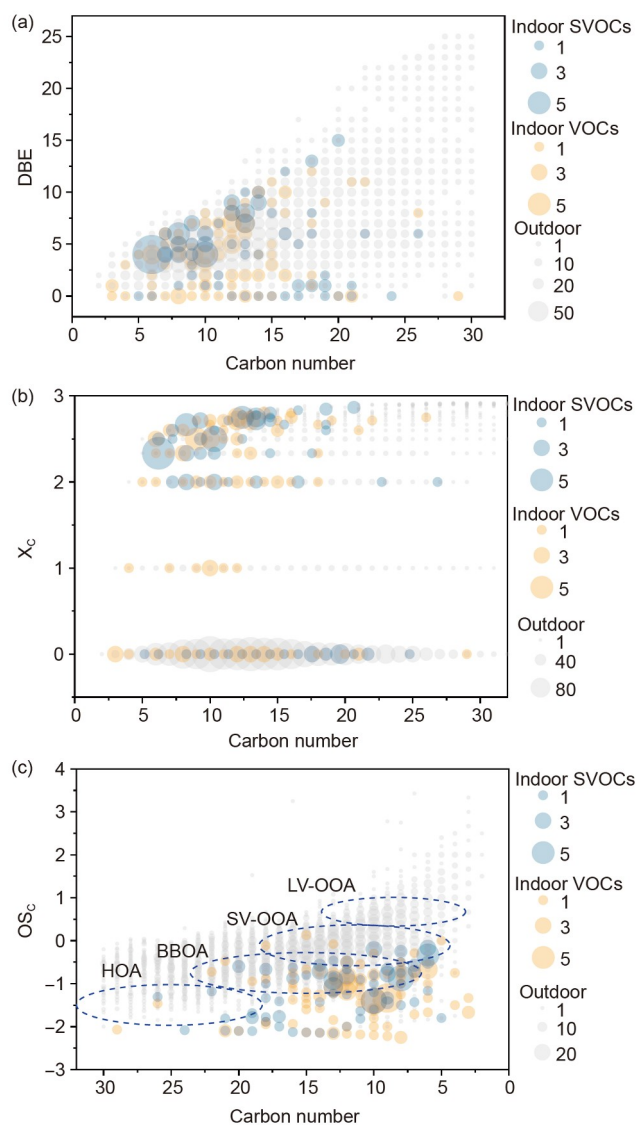
The molecular nature of the SVOC species in the museum was further compared with outdoor air using several chemical metrics. The chemical composition of outdoor aerosols in Beijing was investigated by Steimer et al. [80] using NTA methods with HRMS instruments. Since the organic aerosols were intermediate, which were often formed from gas-phase precursors and finally returned, in part, to gas-phase products [81], their data were used in the comparison. Although their sampling and analytical instruments may have resulted in the inclusion of more compounds in a wider range, significant differences in chemical characteristics between indoor and outdoor air were still observed due to their different emission sources and environmental conditions. The values of the DBE as a function of the carbon number of compounds are shown in Figure 7(a). The number-weighted averages of DBE in indoor air and outdoor air were 5.03 and 7.24, respectively. The results show that there were more unsaturated compounds in the atmosphere than in indoor air. Previous study also found that the indoor VOCs were more saturated than those in outdoor air [16]. The  $X_C$  value of



**Figure 6** (a) Venn diagram showing the relative number distributions of SVOCs detected in museum and house dust. The overlapping areas represent the percentage of SVOCs detected in both types of dust samples. (b) Histogram of the number of SVOCs detected in each chemical class in museum and house dust.

unsaturated SVOCs in indoor air was found to be higher, with an average value of 1.93, as compared with the compounds in outdoor air with an average value of 1.05. As shown in Figure 7(b), the results indicated that there were much more aromatics ( $X_C \geq 2.5$ ) in the museum than that in the atmosphere. These indoor aromatics may come from plasticizers, pesticides, antioxidants, and other emission sources in the museum (Table S1).

The number-weighted  $OS_C$  values of outdoor and indoor air pollutants were found to be  $-0.16$  and  $-1.05$ , respectively, indicating that the outdoor air consisted of relatively more oxidized compounds. It may be due to the typically higher concentration levels of oxidants outdoors than indoors, such as ozone, chlorine, nitrate, and hydroxyl radicals, along with the photolytic action of sunlight [82], which led to more oxidation processes. As shown in Figure 7(c), the majority of outdoor pollutants belonged to the categories of hydrocarbon-like organic aerosol (HOA), biomass-burning organic aerosol (BBOA), semi-volatile oxygenated organic aerosol (SV-OOA), or low-volatility oxygenated organic aerosol (LV-OOA) [56], while many indoor pollutants did not. The findings showed a significant difference between the molecular nature of the SVOC species in the museum and that in the outdoor air. Outdoor air pollutants are primarily generated from vehicle emissions, industrial or agricultural



**Figure 7** Plots of the (a) DBE, (b) aromaticity equivalent ( $X_C$ ), and (c) carbon oxidation state ( $OS_C$ ) as a function of carbon number for the detected indoor SVOCs in the museum and compounds in outdoor air reported in the literature. The size of the bubbles represents the number of compounds.

combustion, and they undergo more intense photochemical reactions. However, indoor air pollutants are primarily derived from building renovation, exhibit materials, maintenance and restoration of artifacts, ventilation, and human emissions. A study conducted by Price et al. [83] at the Colorado Museum of Art found that the reduction of organic pollutants in indoor air was high, with a low number of carbon atoms, which is similar to the findings of the current study.

### 3.5 Limitations

This study had several limitations. First, only four air sampling sites and two dust sampling events were included.

More samples are necessary for an overall understanding of the SVOCs in museum environments. Second, chemical isomers were difficult to differentiate when the differences in SI values, HRF values, and  $\Delta RI$  were subtle, which is a common challenge in NTA studies [48]. Third, only a limited number of chemical reference standards were used to confirm and quantify the hundreds of detected compounds due to the unavailability and high cost of chemical standards, similar to a number of NTA screening studies [43,54,84]. Due to the lack of chemical concentration values, peak abundance was used to represent the environmental concentration of each chemical for data analysis, which may cause uncertainties in comparison of SVOC concentrations in the museum. Next, atmospheric organic aerosol data were used when comparing indoor and outdoor air, because no raw data of NTA studies on outdoor gas-phase SVOCs in Beijing were found, although organic aerosol was an intermediate, which was often formed from gas-phase precursors and ultimately returned, in part, to gas-phase products [81]. Finally, ultrasonication with DCM and methanol was used for extraction in the present study. Since extraction approaches and solvents may influence NTA results, more extraction methods and more types of solvents could be included to avoid the loss of compounds in future studies [48].

## 4 Conclusions

This study is the first of its kind to comprehensively characterize SVOCs in a museum environment using an automatic NTA screening approach with the GC-Orbitrap-MS. Approximately 160 chemicals were identified, most of which were reported in museum environments for the first time. They were found to be associated with the materials used in furnishings and the chemical agents applied in conservation treatment. The results of HCA suggested that spatial variations of indoor gaseous SVOCs existed in the museum, but there were no obvious temporal changes of SVOCs in the indoor dust. Spearman's rank-order correlation analysis showed that several classes of SVOCs were well correlated within each group, as well as between different chemical classes, suggesting their common sources. Fragrances, plasticizers, and softeners/conditioners were found to be the primary sources of SVOC pollution in the museum. Compared with outdoor air, the indoor SVOCs had a lower level of unsaturation and more portions of reduced compounds, which was attributed to the differences in environmental conditions, oxidant levels, and emission sources between indoor and outdoor air. We expected that many of the SVOCs detected in the present study are likely to be present in other similar museum environments. Therefore, the results can be used directly in future studies to confirm and prioritize the SVOC contaminants that may largely contribute to the

overall abundance and have potential impacts on cultural heritage artifacts, museum personnel, and visitors.

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## Supporting Information

The supporting information is available online at [tech.scichina.com](http://tech.scichina.com) and [link.springer.com](http://link.springer.com). The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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