SUPPLEMENTARY INFORMATION (SI)

Description for Pollutant Standards Index (PSI)

Pollution Standards Index (PSI) provides accurately and easily understandable information about air quality. As per National Environment Agency (NEA) of Singapore PSI ranges 0-50, 51-100, 101-200, 201-200 and above 300 corresponds to good, moderate, unhealthy, very unhealthy and hazardous air quality, respectively.

Computation of PSI

Using a network of air quality monitoring stations located in different parts of Singapore, six pollutants particulate matter (PM$_{10}$), fine particulate matter (PM$_{2.5}$), sulfur dioxide (SO$_2$), carbon monoxide (CO), ozone (O$_3$) and nitrogen dioxide (NO$_2$) are measured. These pollutants are used to determine the PSI Value. For each pollutant, a sub-index is calculated from a segmented linear function that transforms ambient concentrations onto a scale extending from 0 through 500. The PSI reading is the highest of the five PSI sub-indices. The PSI is not a composite or an average of the five PSI sub-indices. The breakpoints used in defining each of the six pollutant sub-indices are listed at website of NEA of Singapore. Also, health advisory recommended by NEA of Singapore based on PSI values is also given at the website.

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*a* National Environmental Agency (NEA) Singapore haze website retrieved on 1 May 2017 from http://www.haze.gov.sg


*c* NEA of Singapore website retrieved on 21 June 2017 from http://www.haze.gov.sg/air-quality-information
Chemical Extraction and Analysis

Microwave-assisted extraction method was used for analyzing the particulate matter (PM) filters collected at the three haze levels for total particulate-phase trace elements study. For this purpose, half of the PTFE (Polytetraflouroelthylene) filters was put in the Teflon vessel and 4 ml HNO₃, 2 ml H₂O₂, and 0.2 ml HF were added to it for the extraction of elements (Karthikeyan et al., 2006). The samples were then subjected to digestion with a closed vessel microwave digestion system (MLS-1200 mega, Milestone Inc., Italy) for about 20 minutes. All digested samples were then filtered through 0.45 µm Teflon membrane filters, and sample extracts were diluted to 15 ml with ultra-pure water. The rest of PTFE filter was extracted once in 15 mL Milli-Q water using an ultrasonic bath (Elmasonic S-60H, Germany) at 60°C for 1 h, and then filtered through a 0.45 µm PTFE syringe filter. Total 24 elements (Al, As, Ba, Be, Bi, B, Cd, Cs, Cr, Co, Cu, Ga, Fe, Pb, Li, Mn, Ni, Rb, Se, Sn, Te, Tl, Sn, and Zn) were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700 Series, Agilent Technologies, USA) for both total and water-soluble elements analysis with a sample flowrate of 1 ml minute⁻¹ and the waste was removed from the nebulizer through a peristaltic pump. Field blank values were also processed using the same method and were subtracted from sample concentrations. Moreover, NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) standard reference material, SRM 1648a (urban dust) (12 mg) was analyzed for recovery test for the QA-QC purpose. Further details about ICP-MS standards and SRM materials are provided in the following section.
**QA-QC Protocol**

The ICP-MS standards from high purity standards, USA were used for calibration. The certified values of elements in SRM1648a were: Al (34300 ±1300 mg kg\(^{-1}\) (ppm)), As (115.5 ± 3.9 mg kg\(^{-1}\) (ppm)), Cd (73.7 ± 2.3 mg kg\(^{-1}\) (ppm)), Co (17.93 ± 0.68 mg kg\(^{-1}\)), Cr (402 ± 13 mg kg\(^{-1}\) (ppm)), Cu (610 ± 70 mg kg\(^{-1}\) (ppm)), Fe (39200 ±2100 mg kg\(^{-1}\) (ppm)), Mn (790 ± 44 mg kg\(^{-1}\) (ppm)), Ni (81.1 ± 6.8 mg kg\(^{-1}\) (ppm)), Pb (6550 ± 330 mg kg\(^{-1}\) (ppm)), Rb (51 ± 1.5 mg kg\(^{-1}\) (ppm)), Sr (215 ± 17 mg kg\(^{-1}\) (ppm)) and Zn (4800 ± 270 mg kg\(^{-1}\) (ppm)).

One set of standards (100 µg ml\(^{-1}\)) containing all the 24 elements were prepared in 50 ml by dilution with ultrapure water. Working standards were prepared in the range of 0, 2, 5, 10, 20, 50, 100, 200, 500 and 800 ppb (µg l\(^{-1}\)).

**Recovery for Total Elements**

Analytical recovery of target elements on Standard Reference Material (SRM 1648a) Urban Particulate Matter was estimated by comparing the results of elements in extracted samples of SRM 1648a with the certified values from the National Institute of Standards and Technology (NIST) based on the Eq. (S1):

\[
\text{Concentration Obtained from Extracted Sample} \times 100\% = \frac{\text{Concentration from NIST Certified Values}}{\text{S1}}
\]

In total, four SRM samples were analysed and the recoveries of the elements were in the range of 80 to 110% for total elements with the exception of Cr whose recovery can be improved with the use of ultra-pure HF for the extraction. These values were within the
acceptable range recommended by the Association of Analytical Communities (AOAC, 2002); an appropriate correction factor was used for the estimated recovery of Cr based on the AOAC guideline values. It should be noted that the recovery was calculated only for the 13 elements (as mentioned in the previous section) based on certified values given by NIST for SRM1648a. However, recovery for the remaining 11 elements remains unknown due to unavailability of certified values for these elements.

**Estimation of Deposition Fraction**

The International Commission on Radiological Protection developed the human respiratory tract (HRT) model (ICRP, 1994), a simple and reliable semi-empirical model to estimate inhalation dosimetry (Aleksandropoulou and Lazaridis, 2013). In the present study, the estimation of inhaled and deposited particles in the human respiratory tract was estimated by means of the simplified equations presented by Hinds (1999) and Megido et al. (2016), which fitted the HRT model for ideal spherical geometry particles of standard density.

The inhalable fraction ($f_i$) was estimated in percentage terms using the following Eq. (S2):

$$f_i = \left(1 - 0.5 \cdot \frac{1}{1 + 0.00076d_p^{2.8}}\right) \cdot 100$$  \hspace{1cm} (S2)

Where, $d_p$ is the particle mean diameter in $\mu$m.

Inhaled particles may be deposited in three regions in the human respiratory tract: head (HA), trachea-bronchial (TB) and alveolar (AL). The deposited fractions in each region
(i.e. $f_{d,HA}$, $f_{d,TB}$ and $f_{d,AL}$, respectively) in percentage terms are given by means of the following expressions (S3-S5):

\[
  f_{d,HA} = f_i \left( \frac{1}{1 + \exp(6.84 + 1.183 \cdot \ln d_p)} + \frac{1}{1 + \exp(0.924 - 1.885 \cdot \ln d_p)} \right)
\]  

(S3)

\[
  f_{d,TB} = \left( \frac{0.352}{d_p} \right) \left[ \exp\left( -0.234 \cdot (\ln d_p + 3.40)^2 \right) + 63.9 \cdot \exp\left( -0.819 \cdot (\ln d_p - 1.61)^2 \right) \right]
\]

(S4)

\[
  f_{d,AL} = \left( \frac{1.55}{d_p} \right) \left[ \exp\left( -0.416 \cdot (\ln d_p + 2.84)^2 \right) + 19.11 \cdot \exp\left( -0.482 \cdot (\ln d_p - 1.362)^2 \right) \right]
\]

(S5)

**Potential Human Health Risk Assessment**

Potential human health risk assessment was conducted to estimate health hazards associated with inhalation exposure to PM-bound toxic elements during the hazy days. A comprehensive approach comprising four basic steps (hazard identification, exposure assessment, dose-response assessment, and risk characterization) was used for potential health risk assessment due to toxic elements (USEPA, 2017). The potential health risk results for current work are applicable to the adult population in Singapore. For hazard identification, Al, As, Be, Cd, Co, Cr, Cu, Mn Ni, Pb and Zn were identified as possible trace elements that can cause non-carcinogenic health effects. Similarly, As, Be, Cd, Co, Cr, Ni and Pb were identified as possible elements that can cause carcinogenic health effects (Lu et al., 2014; ATSDR, 2017; USEPA, 2017).
For exposure assessment, the exposure dose of these elements was calculated using Eq. (S6), where CDI is the chronic daily intake concentration of the elements (mg kg\(^{-1}\) day\(^{-1}\)); E is deposition fraction which is assumed to be 0.59, 0.46 and 0.26 for coarse, accumulation and quasi-ultrafine (q-UF) particles based on equations and values given in literature (Volckens and Leith, 2003; Behera et al., 2015); C is the trace element concentration (mg m\(^{-3}\)); ET is exposure time (16 h day\(^{-1}\) for indoors and 8 h day\(^{-1}\) for outdoors); EF is exposure frequency (80 days year\(^{-1}\) as the duration of the 2015 smoke haze was about 80 days in Singapore and this duration was used for calculations considering the worst-case scenario); ED is exposure duration (52 years for adults considering their age from 18 to 70 years); ADAF is age-dependent adjustment factor (1 for adults); IR is inhalation rate (20 m\(^3\) day\(^{-1}\) for adults); AT is average life time (70 years for adults); BW is body weight (70 kg for adults).

\[
CDI = E \times \frac{C \times ET \times EF \times ED \times ADAF \times IR}{AT \times BW}
\]  

For dose-response assessment, chronic reference dosage (RfD, mg kg\(^{-1}\) day\(^{-1}\)) and cancer slope factor (SF, kg day mg\(^{-1}\)) for toxic and carcinogenic elements were calculated using Eqs. (S7) and (S8), respectively. Reference concentration (RfC) for chronic inhalation exposure and inhalation unit risk (IUR) data used in these equations for the elements are obtained from the literature (Lu et al., 2014; USEPA, 2017) and reported in Tables S1 and S2.

\[
RfD = \frac{RfC \times IR}{BW}
\]  

(S7)
\[ SF = \frac{IUR \times BW}{IR} \]  \hfill (S8)

For risk characterization, the health quotient (HQ) and excess lifetime cancer risk (ELCR) were quantified by using Eqs. (S9) and (S10), for potential non-carcinogenic and carcinogenic health risks, respectively.

\[ HQ = \frac{CDI}{RfD} \]  \hfill (S9)

\[ ELCR = CDI \times SF \]  \hfill (S10)

The acceptable limit for HQ is 1, HQ higher than 1 is indicative of adverse health effects for the exposed population while the threshold for ELCR is 1 in a million (i.e., 1.0 \times 10^{-6}). If the exposure risk is above the threshold value, it is of health concern as it may cause a reduction in the life expectancy of exposed individuals.
**Reference Concentration (RfC) and Inhalation Unit Risk (IUR) Data**

**Table S1.** Reference concentration (RfC) for elements for non-carcinogenic risk assessment (Lu et al., 2014; USEPA, 2017).

<table>
<thead>
<tr>
<th>Element</th>
<th>RfC (mg m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.90 \times 10^{-3}</td>
</tr>
<tr>
<td>As</td>
<td>1.05 \times 10^{-3}</td>
</tr>
<tr>
<td>Be</td>
<td>2.00 \times 10^{-5}</td>
</tr>
<tr>
<td>Cd</td>
<td>2.00 \times 10^{-5}</td>
</tr>
<tr>
<td>Co</td>
<td>2.00 \times 10^{-5}</td>
</tr>
<tr>
<td>Cr</td>
<td>1.00 \times 10^{-4}</td>
</tr>
<tr>
<td>Cu</td>
<td>1.41 \times 10^{-1}</td>
</tr>
<tr>
<td>Mn</td>
<td>5.01 \times 10^{-5}</td>
</tr>
<tr>
<td>Ni</td>
<td>7.21 \times 10^{-2}</td>
</tr>
<tr>
<td>Pb</td>
<td>1.23 \times 10^{-2}</td>
</tr>
<tr>
<td>Zn</td>
<td>1.05 \times 10^{0}</td>
</tr>
</tbody>
</table>

**Table S2.** Inhalation unit risk (IUR) for elements for carcinogenic risk assessment (Lu et al., 2014; USEPA, 2017).

<table>
<thead>
<tr>
<th>Element</th>
<th>IUR (m^3 mg^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>4.3</td>
</tr>
<tr>
<td>Be</td>
<td>2.4</td>
</tr>
<tr>
<td>Cd</td>
<td>1.8</td>
</tr>
<tr>
<td>Co</td>
<td>9 (2.8)*</td>
</tr>
<tr>
<td>Cr</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>0.24</td>
</tr>
<tr>
<td>Pb</td>
<td>0.012</td>
</tr>
</tbody>
</table>

* The value for IUR for Co is 9 m^3 mg^{-1} as per USEPA 2017 while it is 2.8 m^3 mg^{-1} as reported by Lu et al. (2014). The higher value was assumed for calculation of potential health risk as a conservative approach.
Uncertainty analysis for input exposure parameters was conducted in order to refine the potential carcinogenic health risk and assess extreme values for policy development. For this purpose, probabilistic approach is considered. The most common example is the Monte Carlo (MC) technique where probability density functions are assigned to each parameter, then values from these distributions are randomly selected and inserted into the exposure equation. After this process is completed many times, a distribution of predicted values results that reflects the overall uncertainty in the inputs to the calculation. The principal advantage of the Monte Carlo method is its very general applicability. There is no restriction on the form of the input distributions or the nature of the relationship between input and output; computations are also straightforward (USEPA, 1992).

Therefore, five input exposure parameters (as mentioned earlier in potential health risk section), namely, exposure frequency (EF), exposure duration (ED), average life time (AT), inhalation rate (IR) and body weight (BW) were considered variables. To estimate probabilistic health risk, these parameters were assumed to follow lognormal distribution and Python language was used to perform MC simulations (Chiu and Slob, 2015; Shao et al., 2017). Constant values of the exposure parameters (as described in the previous section of potential health risk estimate) are assumed as mean values for the lognormal distribution while standard deviations are assumed as 20% of the mean values as a reasonable estimate. Table S3 represents mean values and standard deviations of these
parameters. Results obtained from the output file were then analyzed to estimate 50\textsuperscript{th} and 95\textsuperscript{th} percentile values of potential health risk.

**Table S3.** Mean values and standard deviations assumed for the lognormal distribution of the exposure parameters to perform MC simulations for probabilistic uncertainty analysis for potential carcinogenic health risk.

<table>
<thead>
<tr>
<th>Exposure Parameter</th>
<th>Mean value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF</td>
<td>80</td>
<td>±16</td>
</tr>
<tr>
<td>ED</td>
<td>52</td>
<td>±10.4</td>
</tr>
<tr>
<td>AT</td>
<td>70</td>
<td>±14</td>
</tr>
<tr>
<td>IR</td>
<td>20</td>
<td>±4</td>
</tr>
<tr>
<td>BW</td>
<td>70</td>
<td>±14</td>
</tr>
</tbody>
</table>
Fig. S1. Haze map and backward trajectory analysis using HYSPLIT model for light-haze level 29 October 2015. The haze map is reproduced from weblink http://asmc.asean.org/home/ (with permission from ASEAN Specialized Meteorological Centre (ASMC)).
**Fig. S2.** Haze map and backward trajectory analysis using HYSPLIT model for moderate-haze level on 20 October 2015. The haze map is reproduced from weblink [http://asmc.asean.org/home/](http://asmc.asean.org/home/) (with permission from ASEAN Specialized Meteorological Centre (ASMC)).
**Assessment of Indoor-outdoor PM for Various Haze Levels**

**Fig. S3.** PM$_{2.5}$ indoor to outdoor ratios (I/O ratios) for different levels of haze. The dashed line represents the mean I/O.
**Fig. S4.** Size-resolved particle mass concentrations for the entire sample set for (a) indoors and (b) outdoors. A, B, C, D and E are PM$_{>2.5}$, PM$_{1.0-2.5}$, PM$_{0.5-1.0}$, PM$_{0.25-0.5}$ and PM$_{<0.25}$, respectively.
**Fig. S5.** Size-resolved I/O ratios for different levels of haze. A, B, C, D and E are PM_{>2.5}, PM_{1.0-2.5}, PM_{0.5-1.0}, PM_{0.25-0.5} and PM_{<0.25}, respectively.
**Deposited Doses in the Respiratory System**

**Fig. S6.** Deposited dose in the three zones of respiratory system for PM$_{2.5}$ under three haze levels for indoors and outdoors.
Chemical Composition of Indoor and Outdoor PM

Fig. S7. Mean indoor and outdoor air concentrations for coarse, accumulation and q-UF particles for the 24 elements under light-haze level.
Fig. S8. Mean indoor and outdoor air concentrations for coarse, accumulation and q-UF particles for the 24 elements under moderate-haze level.
**Fig. S9.** Mean indoor and outdoor air concentrations for coarse, accumulation and q-UF particles for the 24 elements under severe-haze level.
**Enrichment Factor (EF)**

Enrichment factor (EF) for various elements were calculated to identify the elements of crustal and anthropogenic origin by using the following Eq. (S11), and the results are shown in Figs. S10-S11.

\[
EF_x = \left( \frac{\frac{C_{x,p}}{C_{Al,p}}}{\frac{C_{x,c}}{C_{Al,c}}} \right) \tag{S11}
\]

Where, \( EF_x \) is the enrichment factor of an element \( x \), \( C_{x,p} \) and \( C_{Al,p} \) are concentrations of an element \( x \) and \( Al \), respectively, in PM, \( C_{x,c} \) and \( C_{Al,c} \) are their concentrations in average crustal materials (Balasubramanian and Qian, 2004). \( EF > 10 \) indicate a non-crustal source for the elements, while elements of crustal origin have \( EF < 10 \).
Fig. S10. Crustal EF of Zn relative to Al and average composition of the continental crust (Mason, 1966) for the size-fractionated samples collected indoors (I) and outdoors (O) during light-haze (L), moderate-haze (M) and severe-haze (S) levels.
Fig. S11. Crustal EF of the selected trace elements relative to Al and average composition of the continental crust (Mason, 1966) for the size-fractionated samples collected indoors and outdoors during light-haze, moderate-haze and severe-haze levels.
Probability Distribution Function (PDF)

The probability distribution function (PDF) was applied to all the 24 selected elements collected indoors and outdoors during light-haze, moderate-haze and severe-haze levels in Singapore to evaluate the spatial and temporal distribution of the selected 24 elements in PM$_{2.5}$. PM$_{2.5}$ was selected for the temporal and spatial distribution analysis considering it currently has air quality standards. The PDF is a function that describes the relative probability of this random variable taking on a provided value. The probability of a random variable falling within a particular region is given by the Gaussian distribution, which can be described as follows by Eq. (S12):

$$y = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right)$$  \hspace{1cm} (S12)

Where, $y$, $\sigma$, $\sigma^2$, $\mu$ and $x$ represent the PDF, standard deviation, variance, average and atmospheric concentration of each selected element, respectively. As a part of the analysis of random phenomena, skewness was used to measure the asymmetry of the probability distribution of selected elements in PM$_{2.5}$. In the case of unimodal distribution, positive skew represents that the tail on the right side is longer than the left side. This reflects that the mass of the distribution is concentrated on the left of the figure. This will happen when the mean of the selected elemental concentrations is less than its own middle. A temporary low level of selected elements may responsible for this phenomenon. On the other hand, negative skew indicates that the tail on the left side of the PDF is longer than the right side suggesting that the mass of the distribution is concentrated on the right of the figure. If the mean of the selected elemental concentrations is greater than the middle, the
graph will be negative skew. This can be explained by several reasons such as unusually high level of selected elements from long-range transportation or accidental explosions (i.e. only few samples with unexpectedly high concentrations). In case the mean is in the middle, it appears more likely to have a figure of symmetrical Gaussian distribution. This represents a conventional normal distribution without any interruptions from other extreme events i.e. accidental explosions or long-range transportation (Pongpiachan and Iijima, 2016).
Fig. S12. Temporal variations of concentrations of the 24 selected elements in PM$_{2.5}$ collected indoors and outdoors during the light-haze, moderate-haze and severe-haze levels in Singapore. I and O refer to indoors and outdoors, respectively.
Fig. S13. Probability distribution function reflecting spatial variations of concentrations of the 24 selected elements in PM$_{2.5}$ collected indoors and outdoors during the light-haze, moderate-haze and severe-haze levels in Singapore. I and O refer to indoors and outdoors, respectively.
Fig. S14. Uncertainty analysis for total potential carcinogenic human health risk for indoors and outdoors and its comparison with threshold value for the three haze levels for (a) coarse (b) accumulation and (c) q-UF mode.
REFERENCES


