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# Source Identification and Apportionment of Halogenated Compounds Observed at a Remote Site in East Asia

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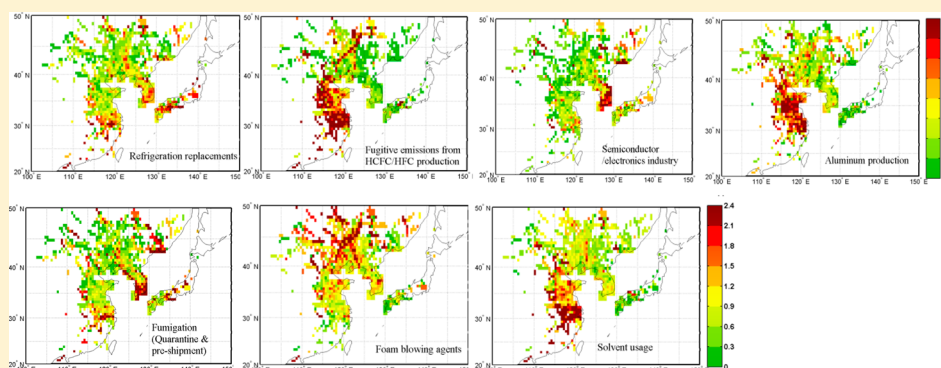
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## S Supporting Information



**ABSTRACT:** The sources of halogenated compounds in East Asia associated with stratospheric ozone depletion and climate change are relatively poorly understood. High-precision in situ measurements of 18 halogenated compounds and carbonyl sulfide (COS) made at Gosan, Jeju Island, Korea, from November 2007 to December 2011 were analyzed by a positive matrix factorization (PMF). Seven major industrial sources were identified from the enhanced concentrations of halogenated compounds observed at Gosan and corresponding concentration-based source contributions were also suggested: primary aluminum production explaining 37% of total concentration enhancements, solvent usage of which source apportionment is 25%, fugitive emissions from HCFC/HFC production with 11%, refrigerant replacements (9%), semiconductor/electronics industry (9%), foam blowing agents (6%), and fumigation (3%). Statistical trajectory analysis was applied to specify the potential emission regions for seven sources using back trajectories. Primary aluminum production, solvent usage and fugitive emission sources were mainly contributed by China. Semiconductor/electronics sources were dominantly located in Korea. Refrigerant replacement, fumigation and foam blowing agent sources were spread throughout East Asian countries. The specified potential source regions are consistent with country-based consumptions and emission patterns, verifying the PMF analysis results. The industry-based emission sources of halogenated compounds identified in this study help improve our understanding of the East Asian countries' industrial contributions to halogenated compound emissions.

## INTRODUCTION

Man-made chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs, transitional substitutes of CFCs) have been widely used in many industrial applications, for example, as foam-blowing agents, aerosol propellants, degreasing solvents, and refrigerants. However, because of their involvement in stratospheric ozone depletion, the production and consumption of these compounds have been regulated by the Montreal Protocol

on Substances that Deplete the Ozone Layer and its Amendments (MP). The MP has defined different schedules to complete phase-out of the production and consumption of these compounds for

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non-Article 5 (mainly developed countries) and Article 5 (developing countries) in consideration of their economic conditions. Consequently, global production and consumption of CFCs have decreased. HCFCs, however, of which consumption in developed countries will be phased out in 2015, are still produced and consumed in developing countries where the regulations start to go into effect in 2013.<sup>1</sup>

As substitutes for CFCs and HCFCs, use of hydrofluorocarbons (HFCs) is expected to increase both in developed and developing countries for many applications where CFCs and HCFCs have been traditionally used.<sup>2</sup> While HFCs are not stratospheric ozone-depleting substances, they are greenhouse gases that make contributions to the Earth's anthropogenic radiative forcing, along with perfluorocarbons (PFCs).<sup>3</sup> The contribution of HFCs to radiative forcing represents about 0.51% of total GHGs radiative forcing from 1970 to 2000, which is dominated by HFC-134a and HFC-23.<sup>2</sup> Hence, these compounds are regulated in Annex I developed countries under the Kyoto Protocol (KP) of the United Nations Framework Convention on Climate Change (UNFCCC). PFCs have been used increasingly since the 1980s in semiconductor and other electronics manufacturing processes, for example, as chamber cleaning and dry etching agents, and are also byproducts of aluminum production.<sup>4</sup> In terms of contributions of chlorine or bromine to stratospheric loading, compounds, such as  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ , and  $\text{CH}_3\text{Br}$ , are also regulated under the MP, but other halocarbons, such as  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ , are not yet regulated.<sup>5</sup>

Because of the strong industrial growth of the East Asia MP Article 5 countries China and Korea their current emissions and changes in emission patterns are of special interest. Recent studies based on atmospheric monitoring have consistently reported a significant increase in the emissions of most halocarbons in East Asia.<sup>6–8</sup> For understanding halocarbon consumption patterns in East Asia, it is important to characterize their chemical speciation, determine their regional baseline concentrations (i.e., background values representing regional clean condition without regional/local pollution events) and calculate their current emission rates. Especially, additional understanding of the regional/industrial source origins and their relative contributions is essential to establish effective regulation strategies. Guo et al.<sup>9</sup> analyzed the source origins, profiles and apportionments of halocarbons using flask sample data from the Pearl River Delta region of China. However, a study on source identifications for a wide range of halogenated compounds observed at a background site in East Asia region has not been performed prior to this work.

The positive matrix factorization (PMF) model has been widely used to identify and apportion sources of atmospheric pollutants.<sup>9–13</sup> PMF uses a least-squares fit to resolve the number of factors controlling the observed time-series of the chemical species of interest by incorporating non-negative data and their errors as point-by-point weights into the optimization process.<sup>10</sup> PMF has been applied in studies of volatile organic compounds (VOCs) and nonmethane hydrocarbons (NMHCs) in urban<sup>12</sup> and remote areas<sup>11,13</sup> and on halocarbons in rural and coastal areas.<sup>9</sup> These studies have identified the primary sources of VOCs and NMHCs and have quantified their relative contributions using PMF models. In this study, we applied a PMF analysis to continuous in situ observations of halogenated compounds made at Gosan, Jeju Island, Korea, from November 2007 to December 2011. The measurement data cover a wide range of halogenated compounds, including CFCs (CFC-11 and CFC-12), HCFCs (HCFC-22, HCFC-141b, and HCFC-142b), HFCs (HFC-23, HFC-134a, HFC-152a, HFC-32, and HFC-125), PFCs ( $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$ ),

sulfur hexafluoride ( $\text{SF}_6$ ), COS, and other chlorinated and brominated compounds ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{Br}$ ).

Here, we attempt to identify and apportion the sources for major halogenated compounds and illustrate their potential source regions using trajectory statistical method coupled with the PMF results. This is first study to identify emission source profiles and potential source regions in East Asia region using an extensive data set of CFCs, HCFCs, HFCs and PFCs observed at Gosan. The results are new information about industry-based emission sources of halogenated compounds monitored at a remote site in East Asia and can help verify bottom-up emission inventories in combination with inverse models. Our findings may also serve as guidelines in establishing regulation strategies for these compounds under the Montreal and Kyoto protocols in East Asia.

## ■ ANALYSIS

**Continuous In situ Measurements.** Ambient concentrations of halogenated compounds have been analyzed every two hours since November 2007 using a gas chromatography–mass selective detector (GC-MS) coupled with an online cryogenic preconcentration system (“Medusa”)<sup>14</sup> at Gosan, Jeju Island, Korea, as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network (see Li et al.<sup>8</sup> for more detailed station information). Daily standard precisions ( $n = 12$ ) are better than 2% for most of the compounds discussed here. The compounds measured here are on calibration scales developed at the Scripps Institution of Oceanography (SIO),<sup>15</sup> with the exception of HFC-125 and  $\text{CH}_2\text{Cl}_2$  that are reported on the UB-98 scale (University of Bristol), HFC-365mfc on the Empa-2003 scale (Swiss Federal Laboratories for Materials Science and Technology) and COS that is linked to the scale of the National Oceanic and Atmospheric Administration (NOAA).

**Data Selection.** For the PMF analysis, we selected 18 halogenated compounds and COS as they are the most abundant compounds with distinctive industrial sources and applications. Among all the measurement data during the period, we selected 2038 data points when all the 19 compounds were detected above the background levels at the same time. During the PMF analysis time air-masses predominantly originate from the northwestern and northeastern directions, which are polluted regions of East Asia. (See Figure S1 in Supporting Information for trajectory residence time analysis). Unlike short-lived, reactive pollutants, halocarbons tend to have significant contributions of global and regional background levels, even for observations in polluted areas in the world, due to their long atmospheric lifetimes. The background concentrations were determined using a statistical method detailed in O'Doherty et al.<sup>16</sup> to exclude influences of trends or variability in the global/regional background levels. The observed enhancements in concentrations from the background values were used in the PMF analysis.

**Positive Matrix Factorization Model Calculation.** The PMF optimization uses a weighted least-squares regression to obtain a best fit to the measured enhancements in the concentration data.<sup>17</sup> Because the main constraints that need to be resolved during the analysis are “source factors”, this is often called a factor analysis. The mathematical expression of the model is given by eq 1:

$$x_{ik} = \sum_{j=1}^p g_{ij} f_{jk} + e_{ik} \quad (i = 1, 2, \dots, m; j = 1, 2, \dots, p; k = 1, 2, \dots, n) \quad (1)$$

where  $x_{ik}$  represents enhanced concentrations in the time series of the “ $i$ ” halogenated compound at the  $k$ th sampling time;  $g_{ij}$  is the

concentration fraction of the  $i$ th compound from the  $j$ th source;  $f_{jk}$  is the enhanced concentration from the  $j$ th source contributing to the observation at the  $k$ th time, which is given in ppt;  $e_{ik}$  is the model residual for  $i$ th compound concentration measured in the  $k$ th sampling time; and  $p$  is the total number of independent sources (i.e., the number of factors).<sup>17</sup> The optimal number of factors ( $p$ ) should be determined by using a function  $Q$ , defined in eq 2

$$Q = \sum_{i=1}^m \sum_{k=1}^n \left( \frac{e_{ik}}{u_{ik} h_{ik}} \right)^2 \quad (2)$$

where  $u_{ik}$  are the uncertainties corresponding to each measurement data point. Following the guideline provided by Polissar et al.<sup>18</sup> for PMF model input uncertainties, we took into account the instrumental measurement uncertainty, monthly standard deviation ( $1\sigma$ ) of background concentration and plus 1/3 of the detection limit value as the overall uncertainty assigned to each data point. The PMF model input uncertainties (in ppt) were constructed as shown in eq 3

$$u_{ik} = \sqrt{u_{ik}^2 + \sigma_{ik}^2} + d_{ik}/3 \quad (3)$$

where  $u_{ik}$  is measurement uncertainties;  $\sigma_{ik}$  is the monthly standard deviation of background; and  $d_{ik}$  is analytical detection limit. The average values of these individual input error terms are listed for all species in Supporting Information Table S1. In eq 2,  $h_{ik} = 1$  if  $|e_{ik}/u_{ik}| < \alpha$ , and otherwise  $h_{ik}$  is defined as  $|e_{ik}/u_{ik}|/\alpha$ . The  $\alpha$  is the outlier threshold distance parameter. Appropriate down weighting of outliers in PMF data sets has been done in many literatures<sup>18–20</sup> by the parameter to reduce the influence of outliers and extreme values. We constrain the PMF analysis with  $\alpha = 4$  that is most commonly used. In other words, when the scaled residual exceeded four times the standard deviation, the uncertainty,  $u_{ik}$ , was increased to “down-weight” that concentration.

The model runs with randomly selected, initial values for  $f$  and  $g$  at a given number of factors ( $p$ ) varying within a range of 2–10 factors to obtain a minimum  $Q$  value at less than 20 iterations.<sup>19</sup> As the number of factors increases, the corresponding minimum  $Q$  values decreases, with a level-off near 6 factors. We carefully examined the solutions with 6, 7, and 8 factors and determined an optimal value based on both goodness of fit to the data and prior knowledge about halogenated compound emissions. The model's goodness-of-fit was estimated from a correlation plot between the measured and model-predicted concentrations. Most of the compounds (16 out of 19 species) showed good correlations ( $R^2 > 0.6$ , see Supporting Information Table S2) for the seven-factor solution. Another way to assess a PMF fit is to examine the distribution of scaled residuals ( $e_{ik}/u_{ik}$ ). We found the most species except COS lie within  $\pm 4$  that is considered as a typical limit (see Supporting Information Figure S2). The six-factor model cannot separate the foam blowing agent sources, which is one of the well-known sources for the halogenated compounds, while the solvent usage source was split in the eight-factor analysis. Therefore, a seven-source model was found to provide the most relevant and meaningful interpretation for the halogenated compounds observed at Gosan. This optimal number of factors allows us to identify seven potential industrial sources in combination with the bottom-up emission information in East Asia for each species. Detailed descriptions of the seven sources are given below in the Results and Discussions section.

**Trajectory Statistics.** The seven sources for halogenated compounds determined from the PMF model were further analyzed to identify their potential source regions by using trajectory statistics, which have often been applied to estimate

potential source areas of air pollutants. Reimann et al.<sup>21</sup> used a statistical analysis coupled with back trajectories for concentrations of individual halogenated species. In this study, we applied the statistical method to enhanced concentrations from the  $j$ th source contributing to the observation at the  $k$ th time (which is denoted as  $f_{jk}$  in eq 1). Since the  $f_{jk}$  values from all seven sources are in a very wide range of concentrations, we need to normalize  $f_{jk}$  values against their time average for  $j$ th source to not bias the statistical significance of one source against the others. Therefore normalized time series of  $f_{jk}$  values were defined as  $m_{jk} = (f_{jk}/(\sum_{k=1}^n f_{jk}/n))$

The underlying assumption of the trajectory statistics method is that elevated concentrations at an observation site are proportionally related to both the average concentrations on a specific grid cell where the observed air mass has been passing over and the residence time staying over that grid cell. Thus, the method simply computes a residence-time-weighted mean concentration for each grid cell by superimposing the back trajectory domain on the grid matrix. The formula is given by

$$\bar{m}_{abj} = \frac{\sum_{k=1}^n (\tau_{abk} m_{jk})}{\sum_{k=1}^n \tau_{abk}} \quad (4)$$

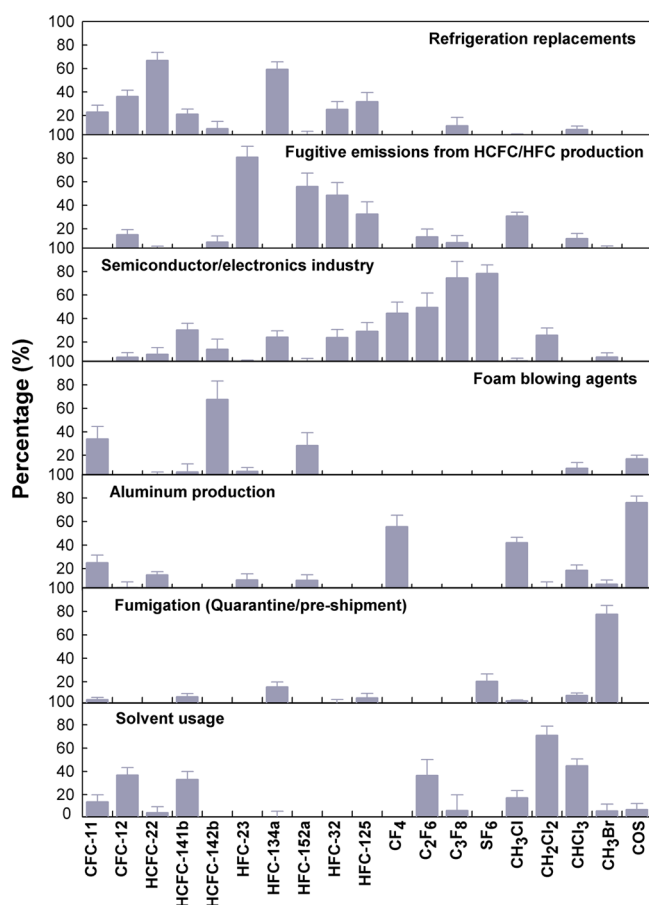
where  $m_{jk}$  is the normalized strength of the  $j$ th source at a given  $k$ th time;  $\tau_{abk}$  is the residence time of the trajectory arriving at Gosan at the  $k$ th time, spent over the grid cell  $a, b$  (in  $0.5^\circ \times 0.5^\circ$ ) within the atmospheric boundary layer; and  $\bar{m}_{abj}$  represent a relative strength of the cell  $a, b$  as a potential source region of the  $j$ th source. Backward trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model of the NOAA Air Resources Laboratory (ARL) using meteorological information from the Global Data Assimilation System (GDAS) model with  $1^\circ \times 1^\circ$  grid cell. HYSPPLIT model was run using 4-day backward trajectories at 500-m altitude above the measurement site (see Figure S4–S6 in Supporting Information for mixed boundary layers at Gosan). The residence times were calculated by the method of Poirot and Wishinski.<sup>22</sup> To eliminate low confidence level areas, a point filter was applied that removed grids where the counts of over passing trajectories were less than 12.<sup>21</sup>

## RESULTS AND DISCUSSIONS

**Seven Sources Identification.** Figure 1 summarizes the source profiles (denoted by  $g$  in eq 1) of 18 major halogenated compounds and COS and uncertainties for the seven factors. The uncertainties were determined from  $1\sigma$  standard deviation of 100 bootstrap replications.<sup>23</sup> The source profiles (i.e., relative abundances of individual species) are used as the final criteria for source identification, suggesting seven sources: refrigeration replacements, fugitive emissions from HCFC/HFC production, semiconductor/electronics industry, foam blowing agents, primary aluminum production, fumigation, and solvent usage.

**Refrigeration Replacements.** The factor, shown in the first panel of Figure 1, explains approximately 67% of HCFC-22 and 59% of HFC-134a enhancements observed. HCFC-22 and HFC-134a are the most abundant species of the HCFC and HFC families, respectively, in the atmosphere. Reflecting their increasing use in refrigeration units and air conditioning systems as CFCs replacements,<sup>5</sup> the baseline values for HCFC-22 and HFC-134a at Gosan have been increasing from 2008 to 2011 by  $\sim 29$  ppt and  $\sim 21$  ppt, respectively. 25% of HFC-32 and 32% of HFC-125 are also explained by this factor, most likely because the compounds are used together in refrigerant blends such as





**Figure 1.** Source profiles of 18 halogenated compounds and COS derived from PMF analysis. The PMF analysis is performed on continuous in situ observations made at Gosan, Jeju Island, Korea, from Nov. 2007 to Dec. 2011. The values in the y-axis are given in concentration contribution percentage (with 1- $\sigma$  standard deviation), so the vertical sum for each species listed on the x-axis is 100.

R410A (HFC-32/HFC-125 = 1:1 by weight) replacing HCFC-22<sup>2</sup>. Note that 22% of total CFC-11 and 36% of total CFC-12 are also explained by this factor, indicating that the CFCs are still emitted from remaining banks in East Asia in refrigeration units. Overall this first factor is related to refrigerant consumption.

**Fugitive emissions from HCFC/HFC production.** The next source factor is distinguished by a high contribution of HFC-23 (ca. 81% of the observed enhancements). HFC-23 is mostly emitted as byproduct during the production of HCFC-22, and ca. 70% of global HFC-23 emissions are from China.<sup>7,8</sup> This source factor also explains 56% of the observed HFC-152a. In general, HFC-152a is used as an aerosol propellant and foam-blowing agent to replace CFCs and HCFCs. However, in China most of the HFC-152a is consumed as chemical feedstock for the production of fluoropolymer (e.g., 1,1-difluoroethene (VDF) and polyvinylidene fluoride (PVDF)).<sup>24</sup> Interestingly, the production rate of HFC-152a in 2009 in China reached 50 kt year<sup>-1</sup>, exceeding the 28 kt year<sup>-1</sup> production of HFC-134a<sup>25</sup> that is most commonly used for refrigeration in the HFC family. Hence, the significant emission rates of HFC-152a reported in several observation studies,<sup>7,8,26</sup> could be related to substantial production of HFC-152a in China. In addition, 48% of HFC-32 and 32% of HFC-125 enhanced concentrations are identified in this factor. Kim et al.<sup>7</sup> and Li et al.<sup>8</sup> already suggested possible fugitive emissions from China due to the significantly high ratio

of HFC-32 vs HFC-125 from what is expected for refrigerant blends (e.g., the ratio ~2.5 ppt/ppt for R410A). This result suggests that emissions of those compounds from colocated halocarbon production facilities may be significant in East Asia, especially in China. Such fugitive emission source must be first identified before they can be taken into account in bottom-up emissions estimates. Fugitive emissions are often excluded from production/consumption type regulations, and thus from bottom-up emission estimations assuming that they do not lead to emissions. However, to preserve the MP's climate benefits by limiting emissions of HFCs,<sup>27</sup> it is critical to make effective regulations for such fugitive emissions.

**Semiconductor/Electronics Industry.** For the third source factor, many species are found to have high contributions: 78% of SF<sub>6</sub>, 74% of C<sub>3</sub>F<sub>8</sub>, 49% of C<sub>2</sub>F<sub>6</sub>, and 44% of CF<sub>4</sub>. SF<sub>6</sub> is widely used in electrical equipment sector as electric insulation materials and also used as etching/cleaning agents in semiconductor/electronics sector.<sup>3</sup> The primary, well-known source of PFCs (foremost CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) is the aluminum industry, however, more recently use of PFCs in the semiconductor/electronics manufacturing for plasma etching and chamber cleaning has been increasing.<sup>4,28</sup> The high correlation between SF<sub>6</sub> and PFCs suggested that this source factor is more related to processes in the semiconductor/electronics industry. Other important compounds related with semiconductor manufacturing such as c-C<sub>4</sub>F<sub>8</sub> (PFC-318) and NF<sub>3</sub> could not be discussed here because their measurement data at Gosan were not available at this point, even though this source factor must have been defined better with their long-term records.

**Foam Blowing Agents.** The fourth source factor is identified by approximately 69% of HCFC-142b, which is the most widely used foam blowing agent for extruded polystyrene boards in place of CFCs.<sup>28</sup> Another foam blowing replacement of CFCs, HCFC-141b does not seem to contribute significantly to this source factor. Interestingly 30% and 33% of HCFC-141b enhanced concentrations are identified in the third (semiconductor/electronics industry) and seventh source factors (solvent usage), respectively. In principle, this compound can be emitted from most of the sources discussed here because of its wide range of uses.<sup>29</sup> However, our analysis seems to suggest that for East Asia HCFC-141b is emitted from banks with fast emission rates, such as dry cleaning agents for electrical equipment and solvents in chemical manufacturing.

**Aluminum Production.** The fifth source factor can be characterized by high percentages of CF<sub>4</sub> (56%) and COS (76%). Emissions of COS mostly occur from coal and biomass burning and various industrial processes including primary aluminum production.<sup>30</sup> The aluminum production industry, particularly in China, is a well-known emission source of PFCs.<sup>4</sup> In this case, both CF<sub>4</sub> and COS seem to share the same emission source, as revealed by a compact correlation of the plot between the observed CF<sub>4</sub> and COS concentrations ( $R^2 = 0.65$ , not shown here). COS is produced from sulfur-containing carbon anodes in the electrolytic systems of aluminum smelters.<sup>31</sup> In addition, it is also possible that coal fired power plants in the vicinity of primary aluminum smelters contribute to this correlation. 42% of CH<sub>3</sub>Cl enhancements seen at Gosan are also attributed to this factor. CH<sub>3</sub>Cl commonly originates from coal burning which similarly to COS could be explained by coal fired power plants in the vicinity of primary aluminum smelters. A recent report also shows that elevated CH<sub>3</sub>Cl concentrations from several Chinese mega cities can be due to use of coal for various industrial activities.<sup>32</sup> The 30% contribution of the second factor (fugitive emission from HCFC/HFC production) to CH<sub>3</sub>Cl may also be explained by coal-fueled production activities.

**Table 1. Seven Industrial Source Factors of Halogenated Compounds Identified by PMF Analysis and Their Relative Source Contributions to the Observations at Gosan in Korea<sup>a</sup>**

factor no.	source profiles	source contributions (%)				
		all observations	CFCs	HCFCs	HFCs	PFCs
factor 1 (HCFC-22 dominant)	refrigeration replacements	9 ± 1	16 ± 3	25 ± 4	20 ± 3	2 ± 1
factor 2 (HFC-23 dominant)	fugitive emissions from HCFC/HFC production	11 ± 1	5 ± 1	4 ± 1	46 ± 5	4 ± 1
factor 3 (SF <sub>6</sub> dominant)	semiconductor/electronics industry	9 ± 1	2 ± 1	14 ± 4	14 ± 3	38 ± 6
factor 4 (HCFC-142b dominant)	foam blowing agents	6 ± 1	6 ± 3	14 ± 6	4 ± 1	0.0
factor 5 (COS dominant)	aluminum production	37 ± 2	32 ± 7	16 ± 4	14 ± 4	37 ± 6
factor 6 (CH <sub>3</sub> Br dominant)	fumigation (quarantine/preshipment)	3 ± 1	1 ± 1	1 ± 1	1 ± 1	1 ± 0.3
factor 7 (CH <sub>2</sub> Cl <sub>2</sub> dominant)	solvent usage	25 ± 3	38 ± 7	26 ± 6	1 ± 1	18 ± 4

<sup>a</sup>The uncertainties were propagated from the errors of  $f$  and  $g$  values. The related formula is given in the text.

**Fumigation (Quarantine and Preshipment).** The sixth factor is identified by approximately 77% of CH<sub>3</sub>Br, whereas the contributions for most other halogenated compounds are negligible. CH<sub>3</sub>Br is released by both anthropogenic and natural processes: agricultural and industrial fumigation, biomass burning, and oceanic production.<sup>5</sup> CH<sub>3</sub>Br is in a poor correlation with CHBr<sub>3</sub>, an ocean source tracer (not shown here), reflecting negligible influence of oceanic source. Given that the contribution of this factor to CH<sub>3</sub>Cl was also negligible, enhanced CH<sub>3</sub>Br levels observed at Gosan are less likely related to biomass burning. Dominant anthropogenic emissions of CH<sub>3</sub>Br are from fumigant related sources. Fumigant consumption has been phased out for MP's non-Article 5 countries by 2010 but for Article 5 countries the use is still permitted until 2013. However, CH<sub>3</sub>Br fumigation use in "quarantine" and "pre-shipment" treatments (QPS) is even exempt for all countries under the MP.<sup>5</sup> UNEP<sup>33</sup> reported that CH<sub>3</sub>Br consumption in QPS treatments was more significant in East Asia countries (China, Korea and Japan) during the sampling period than in any other fumigation uses. Furthermore, Blake et al.<sup>34</sup> already showed during the TRACE-P campaign in 2001 that these QPS applications contribute significantly to CH<sub>3</sub>Br pollution, observed particularly from Korea and Japan. Hence, the high contribution of CH<sub>3</sub>Br in the sixth factor is most likely explained by fumigation use in quarantine/preshipment treatments.

**Solvent Usage.** The seventh and final source factor is identified by high contribution of CH<sub>2</sub>Cl<sub>2</sub> (71%). CH<sub>2</sub>Cl<sub>2</sub> is widely consumed as feedstock, cleaning material and solvent in chemical manufacturing of HCFC-22, plastics, and pharmaceutical products.<sup>35</sup> Since use of CH<sub>2</sub>Cl<sub>2</sub> as industrial solvent often leads to immediate emission to the atmosphere, in contrast to other sources, CH<sub>2</sub>Cl<sub>2</sub> is suggested as an emission tracer for industrial solvents.<sup>36</sup> This factor also represents 45% contribution of CHCl<sub>3</sub> pollution, a compound used as solvent in the pharmaceutical industry.<sup>37</sup> CFC-12, HCFC-141b, and C<sub>2</sub>F<sub>6</sub> that are used as industrial cleaning solvents also show more than 30% contribution. Overall, we can classify this last source as solvent usage from chemical manufacturing industry.

**Relative Contributions of the Seven Sources.** We can estimate the relative contribution of each source to the total elevated concentration of all the halocarbons measurements at Gosan by taking a ratio of time-integrated sum of  $f_{jk}$  values at all  $k$  times for each  $j$  against sum of all enhancements during the sampling period,  $k$ :  $\sum_{k=1}^n f_{jk} / \sum_{j=1}^p \sum_{k=1}^n f_{jk}$ .

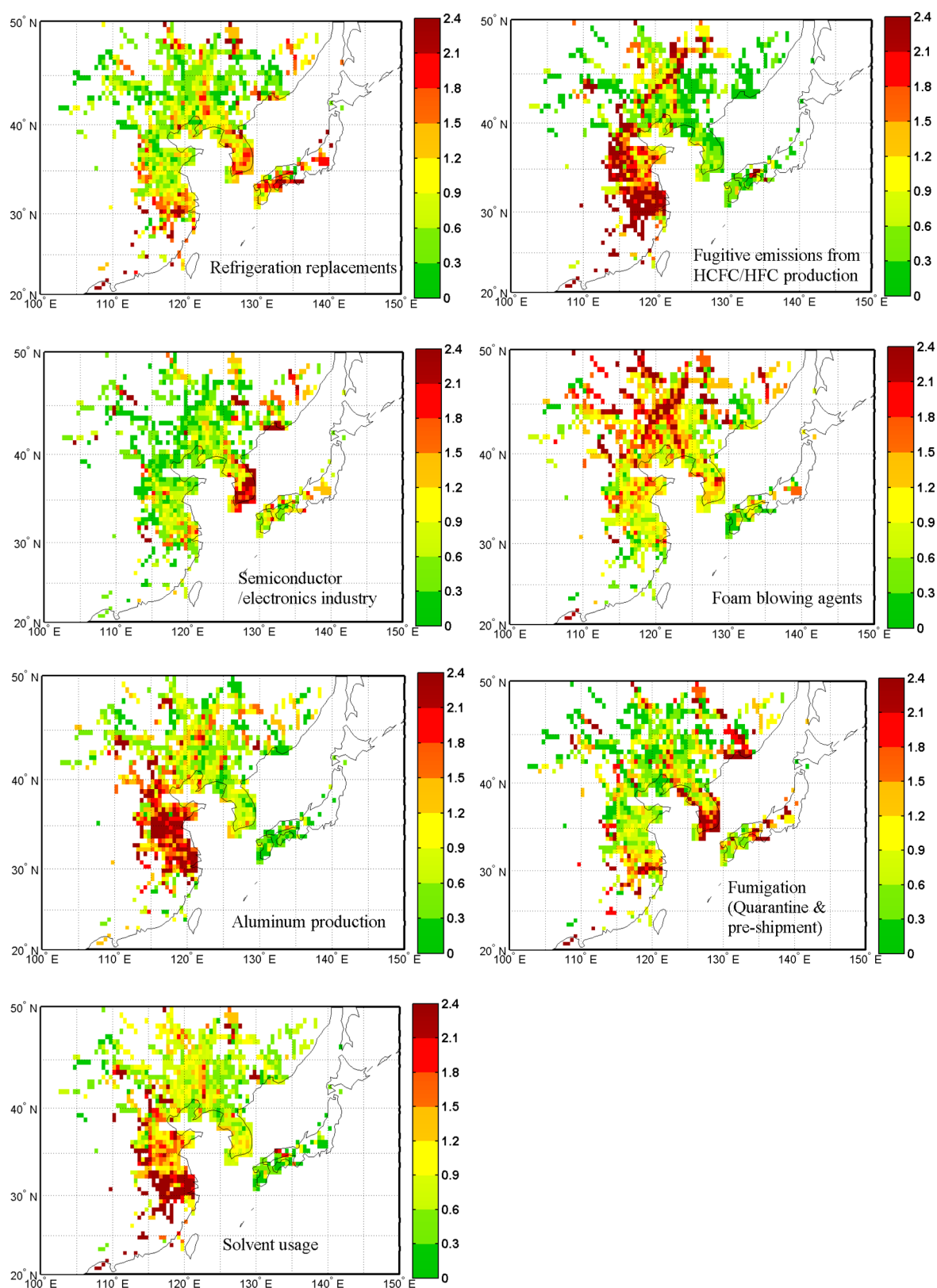
The results are listed in Table 1. The primary aluminum production related source represents the most significant contribution (37 ± 2%; the uncertainty includes errors propagated from  $f$ -value uncertainties) to total halogenated compounds elevated concentrations transported to Gosan; 25 ± 3% of the

contributions were explained by solvent usage related sources; fugitive emissions from production, refrigeration replacement and semiconductor/electronics industry followed with 11 ± 1%, 9 ± 1%, and 9 ± 2%, respectively; 6 ± 1% originated from foam blowing agents sources. In addition, fumigation related sources contributed 3 ± 1%.

Another interpretation of our PMF analysis is which factors are the dominant sources for each halocarbon family (Table 1), we calculated relative contributions of each family compound for each  $j$ th source to sum of all enhancements during the sampling period,  $k$  (for instance, CFCs, HCFCs, HFCs, and PFCs). The formula is  $\sum_{i=1}^m \sum_{k=1}^n g_{ijk} f_{jk} / \sum_{j=1}^p \sum_{k=1}^n f_{jk}$ . The HFC enhancements were mainly characterized by fugitive emissions from HCFC/HFC production-related (46 ± 5%; the uncertainty includes errors propagated from  $g$  and  $f$ -value uncertainties) and refrigeration replacements (20 ± 3%) sources; PFC and SF<sub>6</sub> enhancements were mainly affected by the semiconductor/electronics industries (38 ± 6%) and aluminum production industries (37 ± 6%).

**Potential Source Region Distributions.** A statistical analysis combining the identified seven source factors with back trajectories allowed us to map the regional distribution of each source (Figure 2), which demonstrates potential emission regions for each emission source in East Asia. As described in the Trajectory Statistics section, this method has been generally applied to elevated concentrations of a single compound, but in this case to the all the concentration enhancements from an emission source. Thus, to test the methodological consistency, we made the same analysis with enhanced concentrations of representative species for each source factor (i.e., HCFC-22 for factor 1, HFC-23 for factor 2, SF<sub>6</sub> for factor 3, HCFC-142b for factor 4, COS for factor 5, CH<sub>3</sub>Br for factor 6, and CH<sub>2</sub>Cl<sub>2</sub> for factor 7), and found the resulting distributions, which are illustrated in the Supporting Information (Figure S7), basically identical to Figure 2. In other words, the species selected can represent the seven major emission sources of halogenated compounds in East Asian region as relevant tracers. Thus the tracer compounds for the industries or sources may be further used to monitor any changes in emissions from specific sources.

The potential source areas for refrigeration replacements (factor 1) are widely located over China, Korea and Japan. This result suggests that HCFC-22 and HFC-134a refrigeration are now commonly used as CFC substitutes in East Asia. However, fugitive emissions from HCFC/HFC production-related sources (factor 2) are dominated by eastern China region near the Shandong and Jiangsu provinces, where enormous fluorochemical production complexes are located. Note that the HCFC production of China accounted for ~74% of the global total in 2010.<sup>33</sup> Semiconductor/electronics industry sources (factor 3)



**Figure 2.** Distribution of potential source regions calculated from trajectory statistics for the seven factors identified by PMF analysis.

are located mainly in South Korea, where semiconductor and liquid crystal display manufacturing are known to use both  $\text{SF}_6$  and PFCs.<sup>38</sup> The foam blowing agent sources (factor 4) seem to be located over Korea and China. Given the common use of extruded polystyrene boards filled by HCFC-142b as building

insulators, HCFC-142b is probably consumed for the insulation board foam in these areas. The primary aluminum industry sources (factor 5) are dominated by China. According to the International Aluminum Institute record Chinese primary aluminum production industry contributed ~35% of the global



production in 2009,<sup>39</sup> and thus, the Chinese emissions of PFCs from primary aluminum production are significant. The fumigation sources (factor 6) are most likely associated with anthropogenic emissions occurring in South Korea and active industrial areas near the Yangtze River Delta region in China, where QPS consumption has consistently been reported.<sup>33</sup> Therefore, from the large trade hubs Busan and Incheon, South Korea and Shanghai, China, QPS-related emission of CH<sub>3</sub>Br could be substantial. The solvent usage sources (factor 7) seem to be concentrated in eastern China near Shanghai, which is one of the most industrialized regions in China.

Our statistical analysis was less sensitive to detecting influences from southern China due to the limitation of the back-trajectory domain. Additionally, as noted by Stohl et al.,<sup>40</sup> this method tends to underestimate inherently sharp spatial gradients within the vicinity of the emission hot spots because of its calculation scheme distributing the measured concentrations evenly throughout the grid cells where a trajectory has been passing over. Nonetheless, we found that the source regions identified for the seven factors are all consistent with country-based consumptions and emission patterns,<sup>41,42</sup> which implies that defining source factors and estimating their relative contributions in this study were also reasonable.

In this study, we analyzed industry-based emission source factors of halogenated compounds and their potential source regions using in situ monitoring data obtained at a background site in East Asia. Our results regarding emission source apportionments of halogenated compounds will be further used to validate bottom-up emission inventories and estimates from regional inverse modeling, by calculating the emission rates in combination with air mass transport models. Therefore, continuation of high quality halogenated compounds observation and accumulation of time series data will allow us to monitor their emissions and to detect long-term industrial changes in East Asia.

## ■ ASSOCIATED CONTENT

### Supporting Information

Trajectory residence time, PMF input uncertainties, goodness of the PMF model fit, sensitivity of PMF results to input data uncertainties, mixed boundary layers at Gosan, and potential source region distributions for representative compounds of seven source factors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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