Abstract

We present airborne observations of gaseous reactive halogen species (HCl, Cl2, CINO2, Br2, BrNO2, and BrCl), sulfur dioxide (SO2), and nonrefractory fine particulate chloride (pCl) and sulfate (pSO4) in power plant exhaust. Measurements were conducted during the Wintertime INvestigation of Transport, Emissions, and Reactivity campaign in February–March of 2015 aboard the NCAR-NSF C-130 aircraft. Fifty air mass encounters were identified in which SO2 levels were elevated ~5 ppb above ambient background levels and in proximity to operational power plants. Each encounter was attributed to one or more potential emission sources using a simple wind trajectory analysis. In case studies, we compare measured emission ratios to those reported in the 2011 National Emissions Inventory and present evidence of the conversion of HCl emitted from power plants to ClNO2. Taking into account possible chemical conversion downwind, there was general agreement between the observed and reported HCl: SO2 emission ratios. Reactive bromine species (Br2, BrNO2, and/or BrCl) were detected in the exhaust of some coal-fired power plants, likely related to the absence of wet flue gas desulfurization emission control technology. Levels of bromine species enhanced in some encounters exceeded those expected assuming all of the native bromide in coal was released to the atmosphere, though there was no reported use of bromide salts (as a way to reduce mercury emissions) during Wintertime INvestigation of Transport, Emissions, and Reactivity observations. These measurements represent the first ever in-flight observations of reactive gaseous chlorine and bromine containing compounds present in coal-fired power plant exhaust.

1. Introduction

Reactive halogen species, as oxidizing agents in the troposphere, affect the lifetimes of volatile organic compounds, nitrogen oxides (NOx), ozone (O3), and mercury (Hg) (Saiz-Lopez & von Glasow, 2012) and represent components of the O3 budget (Read et al., 2008; Schroeder et al., 1998). Uncertainties in their sources and multiphase recycling limit accurate assessment of their regional and global impacts on the processes listed above (Rossi, 2003; Simpson et al., 2015). The detection of elevated levels of nitryl chloride (CINO2) in moderately polluted nighttime atmospheres in both marine- and continental-influenced regions (Mielke et al., 2011; Osthoff et al., 2008; Riedel et al., 2012, 2013; Thornton et al., 2010; Young et al., 2012), for instance, has renewed efforts to determine sources of reactive chlorine, which occur mostly in the form of HCl and particulate chloride (pCl). Given the solubility of HCl and its dependence upon particle acidity, HCl and aqueous pCl exist in a thermodynamic equilibrium. Sources of either one, therefore, can influence multiphase chlorine activation chemistry, which leads to CINO2 or Cl2 production (Behnke et al., 1997; Finlayson-Pitts et al., 1989; Roberts et al., 2008; Vogt et al., 1996).
The only available global inventory suggests that approximately 80% of the 62 Tg of gaseous HCl produced per year originates from the ocean (Keene et al., 1999), whereby HCl is displaced from chloride-containing sea salt aerosol to the gas phase with increasing particle acidification (Clegg & Brimblecombe, 1985; Crisp et al., 2014; Robbins et al., 1959). The rest of the global burden is thought to largely originate from combustion processes, including cement production, waste incineration, biomass burning, and coal combustion for electricity generation (McCulloch et al., 1999), as trace amounts of organic and inorganic chloride present within the fuel are converted mostly to HCl during combustion. Anthropogenic HCl emissions are thought to be on a downward trend in the United States over the past few decades, reflecting those of SO2 and consistent with the decline in the use of coal for electricity generation and the implementation of desulfurization technology (United States Office of Energy Markets and End Use), but top-down validation of the emission ratios by direct atmospheric measurements is lacking. On the other hand, the practice of adding halides to coal fuel—mainly as calcium bromide or iodide in solution to curb mercury emissions (Reisch, 2015)—have increased the likelihood of halides being released to the environment. Though elevated bromide levels have been documented in the water environment impacted by the wastewater discharged from coal-fired power plants (Good & VanBriesen, 2016; McTigue et al., 2014; U.S. EPA, 2015), their abundance and composition in the gas exhaust have yet to be determined. Modeling studies on HOCl emissions from power plants have shown significant potential impact on regional photochemistry (Chang et al., 2002; Chang & Allen, 2006; Tanaka et al., 2003); however, speciated measurements of the suite of halogen compounds that are potentially emitted by coal-fired power plants are lacking.

The Wintertime INvestigation of Transport, Emissions, and Reactivity (WINTER) experiment, which utilized the highly instrumented NCAR/NSF C-130 aircraft based out of Norfolk, VA, provided the opportunity to study emissions from power generation plants during the winter season when chemistry and boundary layer dynamics behave differently than during the more often studied summer season. We describe a simple wind trajectory-based approach to attribute each polluted air mass encounter—characterized by sharp enhancements in time of SO2 nearby operational power plants—to one or more potential emission sources. The information documented in the National Emissions Inventory (NEI) 2011 provided a priori estimates of HCl:SO2 emission ratios to compare against those observed during WINTER for the polluted air mass encounters which were able to be attributed to a single operating power plant (https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei). We assess the factors that may have influenced why hydrogen chloride (presumably the most abundant of the chlorine-containing gaseous species emitted from coal combustion) and reactive bromine (Br2, BrCl, and BrNO2) species were measured (or not measured despite elevated SO2 levels) in power plant exhaust.

2. Methods

Mixing ratios of HCl, HOCI, ClO2, CINO2, Br2, BrNO2, BrCl, and SO2 were measured during WINTER using the University of Washington iodide-adduct high-resolution time of flight chemical ionization spectrometer (HRTof-CIMS) aboard the NSF/NCAR C-130 aircraft. The University of Washington HRTof-CIMS instrument is identical in concept to that described by Lee et al. (2014) that flew previously aboard the NOAA P-3 aircraft during the Southeast Nexus campaign (Warneke et al., 2016) but with modifications implemented for the WINTER 2015 experiment. Details of these modifications are provided by Lee et al. (2018). In summary, ambient air is continuously drawn into the HRTof-CIMS through a 40-cm long 1.6-cm inner diameter polytetrafluoroethylene inlet at 22 L/min, resulting in a mean (e-folding) residence time of 0.22 s. In-flight background determinations were conducted every 60 s by overflowing ultrahigh-purity nitrogen (N2) at the entrance of the ion molecule reaction (IMR) region, which we demonstrate represents the dominant surface source of residual signals following encounters of polluted air masses. To reduce the difference in water vapor pressure between ambient measurements and background determinations, which affects the instrument sensitivities (Kercher et al., 2009; Lee et al., 2014), the IMR region was continuously humidified with 100 cm3/min STP of saturated ultrahigh-purity nitrogen N2 flow resulting in about 0.15 torr of constant water vapor pressure in the IMR region. The IMR region is maintained close to 75 torr with a mean residence time of ~30 ms.

Different techniques were employed to determine HRTof-CIMS sensitivity and its dependence on water vapor pressure, depending on availability of the calibrant gas. Cl2 and SO2 were calibrated using...
compressed gas cylinders (10.1 ppm ± 5% SO₂ in N₂, Scott-Marin; 7.5 ppm ± 5% Cl₂ in N₂, Praxair). Br₂ was calibrated using a permeation device (96 ng/min, KIN-TEK) whose output was verified by gravimetric analysis. HOCI was calibrated following the protocol described by Foster et al. (1999). HCl was calibrated using micro-injections of methanol solutions of known HCl concentrations (Sigma-Aldrich), as described by Lee et al. (2014). We relied on the iodide ionization sensitivity to BrNO₂ determined by quantum chemical calculations described by Iyer et al. (2016), scaled by the ratio of the calculated to measured sensitivities to ClNO₂. For BrCl, we applied the mean of the measured sensitivities of Cl₂ (2.9 counts per second per ppt normalized to a million total reagent ion counts per second, or ncps/ppt) and Br₂ (2.0 ncps/ppt) of 2.5 ncps/ppt, which is comparable to the sensitivity obtained by quantum chemical calculation of 3.0 ncps/ppt (Iyer et al., 2016). The dependence of the sensitivity on water vapor pressure was determined by varying the humidity level of the overflow gas into which the calibrate gases were diluted. We estimate a 30% uncertainty for those species that were directly calibrated and 50% for BrNO₂. These levels of uncertainty do not significantly impact the main findings reported below, which are that (i) Br₂, BrNO₂, and BrCl together far exceed—even after accounting for measurement uncertainty—the amount of bromine expected given the observed amounts of chlorine species and typical bromine to chlorie ratios found in U.S. coal and that (ii) such encounters were observed in only the air masses originating from coal-fired power plants without wet flue gas desulfurization (FGD) but not others that employed wet FGD or in exhaust from power plants utilizing fuels other than coal.

The 1-s HRTToF-CIMS detection limits (3σ) for HCl, HOCI, Cl₂, ClNO₂, Cl₂, BrNO₂, BrCl, and SO₂ are 160, 12, 1.2, 1.8, 1.5, 3.0, 2.7, and 500 ppt, respectively. HBr and HOBr were not detected in power plant exhaust due to spectral interferences from high levels of sulfur oxides clustered with the iodide reagent ion that occur at the same nominal masses. Laboratory (Enami et al., 2007; Huff & Abbatt, 2000; Mochida et al., 1998, 2000; Santschi & Rossi, 2005) and field (Neuman et al., 2010) studies report on the potential for rapid heterogeneous conversion of Cl₂, HOCI, or HOBr to yield a range of bromine containing gaseous species. Though we cannot definitively rule out the possibility of these reactions occurring on the surface of the HRTToF-CIMS inlet, it is unlikely that inlet conversion to yield bromine compounds occurred only while sampling the exhaust from coal-fired power plants that were not employing wet FGD technology, as discussed below. Ambient SO₂ was also measured during WINTER by the UV fluorescence technique (Ryerson et al., 1998), and comparison of SO₂ between the two techniques is presented in the manuscript by Lee et al. (2018). The SO₂ data reported here were obtained by the HRTToF-CIMS.

Mass concentrations of total submicron nonrefractory particulate chloride (pCl) and sulfate (pSO₄, including organic sulfates) were observed using a high-resolution time-of-flight aerosol mass spectrometer (DeCarlo et al., 2006; Dunlea et al., 2009). Though the suite of instruments on board the C-130 were not able to resolve chloride in refractory and supermicron particles in power plant exhaust with high enough time resolution, it has been extensively reported that coal chloride is emitted primarily as HCl (Herod et al., 1983; Tillman et al., 2009; Tsubouchi et al., 2018; Vassilev et al., 2000). As such, our approach of estimating an upper limit on gaseous bromine species expected in coal-fired power plant exhaust given the sum of the measured chloride species and the well-established bromide to chloride ratio in U.S. coal is justified, as discussed below. NOₓ and NO were measured using cavity ring-down spectroscopy (Wild et al., 2014), while carbon monoxide (CO) was measured using vacuum ultraviolet (VUV) resonance fluorescence (Aero-Laser). NOₓ was also quantified by two other techniques: (i) by conversion of ambient nitrogen oxides by heated gold catalyst followed by measurement of the resulting NO as well as the ambient NO (Ridley et al., 2004) and (ii) by heating ambient air to 540 °C and subsequently measuring the resulting NO₂ formed as a result of thermal dissociation of nitrogen oxides, as well as the ambient NO₂ (Day et al., 2002; Wooldridge et al., 2010).

3. Results
3.1. Plume Identification and Power Plant Attribution

We identified 50 encounters in which SO₂ mixing ratios were elevated above HRTToF-CIMS detection limit (1-s 3σ of ~500 ppt) over a period of several seconds to few minutes, ensuring robust assessment of emission ratios. Mixing ratios of SO₂, pSO₄, HCl, pCl, ClNO₂, and Cl₂ as well as the altitude and wind direction during one of those encounters are shown in Figure 1. We present the emission ratio of a compound of interest in supporting information Figure S1 only if its abundance is at least 3 times the instrument level of detection (LOD), and it exhibits a minimum correlation (R² ≥ 0.4) with the tracer of interest such as SO₂. The R² of 0.4 was
the cutoff above which the orthogonal least squares fit slope was determined to be statistically robust, defined conservatively as when the ratio of the standard error of the slope to the slope was consistently less than 0.1. The median (25th and 75th percentiles) duration of the 50 encounters was about 1.5 min (0.9 and 3.5 min). Using the criterion described above, pSO4 was the most frequently detected (43 out of 50) of the gaseous or particulate species that was simultaneously enhanced with SO2 (Figure S1). Four of the seven plume encounters without pSO4 were due to a lack of time-of-flight aerosol mass spectrometer data because of routine in-flight sampling strategies such as background determinations. We use the phrase emission ratio for all reported halogen species for consistency, though whether they are formed during combustion like HCl or produced following the release of precursors into the atmosphere is still unclear. Moreover, ambient levels immediately outside of exhaust plumes originating from power plants were typically below instrument detection limits for some species (e.g., Br2, BrNO2, and BrCl), suggesting no other sources in the region. Other species (e.g., pCl, ClNO2, pSO4, and HCl) were on some encounters detected outside of power plant exhaust plumes, indicating additional regional sources. The reported

Figure 1. Mixing ratios of (a) SO2, pSO4; (b) HCl, pCl; (c) ClNO2, and Cl2 during research flight 11 on 9 March around 4 p.m. local time (polluted plume encounter number 44 out of 50; see Table S1). The slopes with respect to SO2 shown in the insets of (a), (b), and (c) define the corresponding emission ratios with respect to SO2. Altitude and wind direction during this polluted air mass encounter are shown in (d).
emission ratios were determined as the enhancement relative to SO2 without forcing the y-intercept to 0, as such, represent only the amount due to power plant emissions.

For each plume encounter, we defined a wind sector in which the SO2 emission source could have resided. This sector originated from the observation point and was drawn initially two transport hours away, determined assuming constant mean wind speed with ±3 standard deviations of the observed wind direction defining the sector boundaries. If the initial sector did not encompass a single operating power plant as reported in the Continuous Emission Monitoring Systems (first quarter of 2015; https://ampd.epa.gov/ampd/) inventory, the sector size was increased by incrementally increasing the transport time by 10 min and angle defining the sector boundaries by 5° until a power plant was captured within the sector. An example of this approach is shown in Figure 2, the wind sector for the polluted air mass encountered on 9 March at around 16:00 (local time) about 150 km east of Pittsburgh, PA. The high levels of SO2 and halogen-containing compounds, high degree of covariance, the direction of the observed winds (Figure 1), and the absence of any other major emission sources in the immediate vicinity (Figure 2) strongly suggest that the intercepted air mass originated from a common source of both species, likely the Homer City power plant, given its proximity (~2.7 km).

Using this wind sector approach, we attributed 12 of the 50 plume encounters to eight unique emission sources (Table 1). The rest (38 out of the 50) were attributed to two or more possible emission sources; that is, more than one power plant source resided in the defined wind sector region. The names of the possible emission source facilities, distances to each from the point of observation, along with the date, time, latitude, longitude, and research flight number of each of the 50 encounters are provided in Table S1, while the observed emission ratios with respect to SO2 are shown in Figure S1.
and observed emission ratios (e.g., CO$_2$:NO$_y$, NO$_y$:SO$_2$, and CO$_2$:SO$_2$) did not provide a clear determination as to which one of the potential power plants in wind sector was responsible for the polluted air mass. Additionally, given the difficulty in modeling plume transport (e.g., using back trajectories) on such fine spatial scales, particularly at nighttime when most of the plume encounters occurred, and the close proximity of many of these power plants to each other relative to the typical variability in the observed wind directions, we did not attempt to parse the list of potential emission sources any further.

Though characterized by elevated levels of SO$_2$ and observed downwind of at least one operational power plant, contributions to the identified polluted air mass encounters from sources other than power plants cannot be completely ruled out. For instance, plume encounter 11 (Figure S2) observed on 24 February during research flight 7 and attributed solely to the Chambersburg Units 11 and 12 facility, which is further upwind of the city of Chambersburg, PA, relative to the point of observation, exhibited higher CO:NO$_y$ ratios (~3 ppb:ppb) relative to the other plume encounters that were attributed to single emission sources (Table S1), suggesting a possible small contribution from urban sources which are characterized by higher CO/NO$_y$ ratios (CO/NO$_y$ of typically ~10 ppb/ppb or higher; Hassler et al., 2016) relative to those of power plants. During plume 11 encounter, mixing ratios of SO$_2$, HCl, CO, and NO$_y$ were all elevated during this descent/ascent maneuver, though the temporal variations in SO$_2$ and HCl were rather distinct from those of CO and NO$_y$, indicating that though the CO:NO$_y$ emission ratio for this plume encounter was elevated, the HCl and SO$_2$ likely originated from a source distinct from the nearby urban center. Such encounters highlight the difficulty in attributing a plume encounter to a specific emission source, particularly an air mass observed in the colder wintertime nighttime atmosphere that contain air mass influenced by a suite of combustion sources under a relatively stagnant, shallow boundary layer. pCl and ClNO$_2$ during plume 11 were more correlated with SO$_2$ and HCl (Figure S2), suggestive of an urban source of pCl and ClNO$_2$. We show examples below of enhancements in pCl and ClNO$_2$ with minimal influence from urban sources.

### 3.2. HCl in Power Plant Emissions

Ambient levels of HCl were elevated above HRToF-CIMS LOD (1-s 3σ of ~180 ppt) and robustly correlated ($R^2 \geq 0.4$) with SO$_2$ in 18 of the 50 identified air mass encounters. We report the emission ratio of a compound relative to SO$_2$ only if this criteria was met (Figure S1). The median (25th and 75th percentiles) HCl:SO$_2$ emission ratio was $3.3 \times 10^{-2}$ ($2.5 \times 10^{-2}$ and $5.3 \times 10^{-2}$) ppb:ppb, the highest compared to those of pCl, Cl$_2$, and ClNO$_2$ (Figure 3). The plume encounters in which each compound was robustly detected ($\geq 3 \times$ LOD and $R^2 \geq 0.4$ with respect to SO$_2$) and the median emission ratio with respect to SO$_2$ for each compound are shown in Figure S1.

<table>
<thead>
<tr>
<th>Plume number</th>
<th>Name of emission source (state)</th>
<th>Fuel utilized</th>
<th>Observed HCl:SO$_2$ emission ratio ± standard error ($R^2$) (ppt:ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>W H Zimmer (OH)</td>
<td>Coal/natural gas</td>
<td>14.5 ± 2.6 (0.15)</td>
</tr>
<tr>
<td>4</td>
<td>P H Gatfelter (OH)</td>
<td>Coal/diesel</td>
<td>7.3 ± 4.6 (0.03)</td>
</tr>
<tr>
<td>11</td>
<td>Chambersburg 12 and 13 (PA)</td>
<td>Natural gas</td>
<td>53.0 ± 1.4 (0.81)</td>
</tr>
<tr>
<td>12</td>
<td>Chambersburg 12 and 13 (PA)</td>
<td>Natural gas</td>
<td>53.1 ± 2.0 (0.73)</td>
</tr>
<tr>
<td>13</td>
<td>Mountain (PA)</td>
<td>Natural gas/distillate fuel oil</td>
<td>74.8 ± 1.2 (0.96)</td>
</tr>
<tr>
<td>39</td>
<td>Jack McDonough (GA)</td>
<td>Diesel/natural gas</td>
<td>23.5 ± 13.2 (0.04)</td>
</tr>
<tr>
<td>40</td>
<td>Jack McDonough (GA)</td>
<td>Diesel/natural gas</td>
<td>8.4 ± 22.4 (0.00)</td>
</tr>
<tr>
<td>41</td>
<td>Jack McDonough (GA)</td>
<td>Diesel/natural gas</td>
<td>17.6 ± 15.6 (0.02)</td>
</tr>
<tr>
<td>42</td>
<td>Harllee Branch (GA)</td>
<td>Coal</td>
<td>35.6 ± 1.4 (0.95)</td>
</tr>
<tr>
<td>43</td>
<td>Harllee Branch (GA)</td>
<td>Coal</td>
<td>27.1 ± 2.7 (0.69)</td>
</tr>
<tr>
<td>44</td>
<td>Homer City (PA)</td>
<td>Coal</td>
<td>28.8 ± 1.3 (0.94)</td>
</tr>
<tr>
<td>45</td>
<td>Mountour (PA)</td>
<td>Coal</td>
<td>0.7 ± 1.1 (0.00)</td>
</tr>
</tbody>
</table>

Note. OH = Ohio; PA = Pennsylvania; GA = Georgia.
Of the 50 polluted air mass encounters, 12 were attributed solely to eight unique emission source facilities (Table 1), using the wind trajectory approach detailed above. Six of those 12 exhibited robust levels of HCl (∼3 × LOD and $R^2 \geq 0.4$). Three of those six were attributed to two power plant facilities (Harllee Branch and Homer City) whose HCl:SO2 emission ratios are reported in the 2011 NEI inventory, allowing a comparison between observations and inventory (Figure S3). Four of the other six plumes were attributed to power plant facilities whose HCl:SO2 emission ratios were not reported in the 2011 NEI inventory (W H Zimmer, Montour, Chambersburg, and Mountain). The remaining two plumes exhibited enhancements of SO2 mixing ratios that were so small, the enhancement in HCl would have been below instrument LOD given the reported HCl:SO2 emission ratios of the source facilities to which they were attributed (P H Glatfelter and Jack McDonough), as shown in Figure S3.

The polluted air masses intercepted downwind of Homer City (plume number 44: 2.7 km, or ~9.0 min assuming constant mean wind speed of 5.0 m/s) and Harllee Branch (plume number 42: 5.2 km, or 19 min assuming constant mean wind speed of 4.4 m/s) exhibited HCl:SO2 emission ratios of $2.9 \times 10^{-2}$ and $3.6 \times 10^{-2}$ ppb:ppb, respectively, with high degrees of correlation between HCl and SO2 (Table 1). The WINTER observed emission ratios were lower by 13% and 28%, respectively, relative to those reported in the 2011 NEI inventory, possibly reflecting a decrease in HCl relative to SO2 emissions from these two sources from the period when the 2011 NEI inventory was compiled to when the WINTER observations were conducted, but these differences are within the calibration uncertainty of the HRToF-CIMS measurements. Additionally, emissions from power plants can vary over short time periods depending on operating conditions such as efficiency of emission control technology, fuel composition (i.e., halide content of coal which can depend on the mine where the coal was extracted, bituminous vs. subbituminous, etc.), and combustion temperature (Frey & Rubin, 1991; Rubin et al., 1997). Thus, emission ratios may vary over time. Nonetheless, the variability in HCl mixing ratios observed across the 18 air mass encounters with robust HCl ($\geq 3 \times$ LOD and $R^2 \geq 0.4$) was reasonably explained by the HCl expected from the product of the median of HCl:SO2 emission ratios of all power plants reported in the 2011 NEI inventory (Figure S4a), regardless of fuel combusted, and the observed SO2 enhanced ($\Delta$SO2) in each of those 18 plume encounters (Figure S4b), as given by equation (1):

$$\Delta HCl = \Delta SO2 \times NEI \left( \frac{HCl}{SO2} \right)$$

where NEI (HCl/SO2) is a representative HCl:SO2 emission ratio. The air mass encounters in which HCl was not robustly detected can readily be explained if the power plant emitted HCl at a ratio to SO2 lower than the median. Power plants tend to be colocated, and reported HCl:SO2 emission ratios from facilities within a spatial cluster can vary over 3 orders of magnitude (Figure S4a). Thus, our observations will be sensitive to the sources in a given region with the highest HCl:SO2 emission ratio and likely represent a cluster average.

HClSO2 emission ratios reported in the inventory are generally derived from the flue gas at the source site (https://www.epa.gov/emc/method-26-hydrogen-chloride-halides-halogens). Airborne observations downwind of the sources, such as those presented here, can be affected by the chemical processing of HCl following its release to the atmosphere. For instance, two air mass encounters both originating from Harllee Branch were intercepted at approximately 5.2 km (plume number 42; Figure S5) and 37.8 km (plume number 43; Figure S6) downwind during the night on research flight 10. The emission ratios with respect to SO2 decreased for HCl and increased for pCl, CINO2, and Cl2 from plume encounters number 42 to 43 (Figure S7). No significant enhancement in CO mixing ratios was observed in either of the plumes (Figures S5 and S6), indicating neither was strongly influenced by urban combustion sources. These observations, therefore, support the production of CINO2 and Cl2 in power plant exhaust, consistent with the findings

![Figure 3](https://www.epa.gov/emc/method-26-hydrogen-chloride-halides-halogens)
of Riedel et al. (2013), with HCl and pCl presumably acting as their precursors. That is, HCl partitions to the particle phase and ClNO2 is produced by heterogeneous reaction involving N2O5 and pCl (Fibiger et al., 2018; Finlayson-Pitts et al., 1989). The decrease in HCl:SO2 between the two plume encounters was $8.5 \times 10^{-2}$ ppb:ppb, while the increase in $(pCl + ClNO2 + 2 \times Cl_2):SO2$ was only $1.8 \times 10^{-3}$ ppb:ppb, indicating that $6.7 \times 10^{-3}$ ppb:ppb of chlorine was lost (Figure S7a) due presumably to the formation of another pool of chlorine reservoir species not quantified by the HRToF-CIMS. HCl loss by deposition in the shallow nocturnal surface layer during the ~9-min transport from the emission source to where the plume was intercepted was likely negligible given that its lifetime with respect to deposition is approximately 1 to 2 days (Graedel & Keene, 1995). HCl and ClNO2 were generally the dominant components of Cl and with the balance shifting toward ClNO2 and away from HCl with increasing abundances of N2O5 and pCl (Figure S8), also consistent with the formation of ClNO2 in power plant exhaust (Riedel et al., 2013).

Correcting the observed HCl:SO2 emission ratio for the Harllee Branch by accounting for HCl loss determined between plume encounters 42 and 43 adds only about 1.2% to the observed emission ratio that is lower than that reported in the 2011 NEI inventory by 28%.

### Table 2

Plume Encounters That Exhibited Elevated Levels of at Least One of the Three Reactive Bromine Compounds (Br2, BrNO2, and BrCl) Detected by the HRToF-CIMS

<table>
<thead>
<tr>
<th>Plume #</th>
<th>RF # date time (EST)</th>
<th>N2O5:SO2 (ppb:ppb)</th>
<th>Distance (km) and time (hr) since emission</th>
<th>Plant(s)</th>
<th>Coal type</th>
<th>SO2 control technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>RF 2/6 February 17:02</td>
<td>$-1.0 \times 10^{-4}$ ppb:ppb 10 ppt</td>
<td>3.8 km 0.3 hr</td>
<td>Gavin</td>
<td>Bituminous, subbituminous</td>
<td>Wet FGD</td>
</tr>
<tr>
<td>9</td>
<td>RF 2/6 February 18:25</td>
<td>$8.0 \times 10^{-4}$ ppb:ppb 29 ppt</td>
<td>6.0 km 0.4 hr</td>
<td>Kyger</td>
<td>Bituminous, subbituminous</td>
<td>Wet FGD</td>
</tr>
<tr>
<td>14</td>
<td>RF 7/24 February 6:52</td>
<td>$-1.1 \times 10^{-2}$ ppb:ppb 670 ppt</td>
<td>11.3 km 0.7 hr</td>
<td>Roxboro</td>
<td>Bituminous, subbituminous</td>
<td>Wet FGD</td>
</tr>
<tr>
<td>16</td>
<td>RF 9/2 March 2:42</td>
<td>$-4.0 \times 10^{-4}$ ppb:ppb 28 ppt</td>
<td>18.0 km 0.9 hr</td>
<td>Seward</td>
<td>Bituminous waste coal</td>
<td>Dry scrubber (#1 and 2)</td>
</tr>
<tr>
<td>21</td>
<td>RF 9/3 March 4:29</td>
<td>$2.0 \times 10^{-4}$ ppb:ppb 86 ppt</td>
<td>54.2 km 2.0 hr</td>
<td>Ebensburg</td>
<td>Waste coal (bituminous)</td>
<td>Reagent injection</td>
</tr>
<tr>
<td>42</td>
<td>RF 11/3 March 3:35</td>
<td>$-7.1 \times 10^{-3}$ ppb:ppb 618 ppt</td>
<td>5.2 km 0.32 hr</td>
<td>Harllee Branch</td>
<td>Bituminous</td>
<td>Dry FGD (Units 1 and 2)</td>
</tr>
<tr>
<td>44</td>
<td>RF 11/9 March 16:00</td>
<td>0 ppb:ppb 2 ppt</td>
<td>2.7 km 0.15 hr</td>
<td>Homer City Generating Station</td>
<td>Bituminous</td>
<td>Dry FGD (Units 1 and 2)</td>
</tr>
</tbody>
</table>

Note: We define Br as the sum of these three species. The times since emission were calculated assuming that the observed wind speed at the plume intercept location remained constant. HRToF-CIMS = high-resolution time of flight chemical ionization spectrometer; FGD = flue gas desulfurization; EST = Eastern Standard Time.
3.3. Bromine in Power Plant Emissions

We identified seven encounters in which Br$_2$, BrCl, and/or BrNO$_2$ were robustly detected ($\geq 3 \times$ LOD and $R^2 \geq 0.4$ with respect to SO$_2$), listed in Table 2. Two of those seven were attributed to a sole source (Homer City, Figures 2 and 4; and Harllee Branch, Figure S5) while the rest were attributed to two or more facilities. All potential sources for these seven air mass encounters utilized coal or waste coal as its primary fuel (https://www.eia.gov/; https://ncrdspublic.er.usgs.gov/coalqual/), except for the Armstrong Power facility (natural gas and diesel), which was one of five potential emitting sources for plume encounter 16 (Table 2). According to the U.S. Energy Information Administration (https://www.eia.gov/coal/data/browser/), none of the potential emitting sources listed in Table 2 reported utilizing refined coal, or coal that had been treated with bromide salts prior to combustion, which can increase the likelihood of higher bromine relative to chlorine emissions, during WINTER observations. Six of the seven plume encounters containing Br$_r$ were attributed to at least one emission source that was not employing wet flue gas desulfurization (Table 1), which efficiently transfers oxidized HgBr$_2$ from gas to liquid phase (McTigue et al., 2014; U.S. EPA, 2015). The exception was air mass encounter number 5, which originated from either the Kyger or Gavin facilities (Figures S9), both of which reported employing wet FGD. The Kyger facility, however, stopped operations on 7 February, the day after the WINTER measurements, which may have impacted the wet FGD operation (ampd.epa.gov/ampd/).

Figure 4. Mixing ratios of (a) Br$_2$, (b) BrNO$_2$, and (c) BrCl observed during the same plume encounter as shown in Figure 1. The insets show the corresponding comparison to SO$_2$.
To assess why Br<sub>y</sub> species were observed in some but not all encounters, we estimate an upper limit to the total amount of reactive bromine compounds (TRB), including those not measured by the HRToF-CIMS, that could have been present in the intercepted air mass (Figure S10) using the equation below:

\[
TRB = \Delta Cl_y \times \text{coal}(Br/Cl),
\]

where the \(\Delta Cl_y\) is the observed enhancement of reactive chlorine species in each plume encounter, and coal (Br/Cl) is the bromide to chloride ratio characteristic of U.S. coal (~0.02) (Granite et al., 2015; Kolker et al., 2012). The encounter with the highest expected TRB that did not contain any detectable amounts of Br<sub>y</sub> was plume encounter number 15, which was observed during nighttime; therefore, loss by photolysis of Br<sub>y</sub> during transport would not explain their absence downwind. The expected TRB given the observed enhancement in Cl<sub>y</sub> for encounter number 15 was \(~148\) ppt (equation (2)), which was greater than the expected TRB of six of the seven encounters in which Br<sub>y</sub> was actually observed. Encounter number 15 was attributed to the Conemaugh facility (Figure S11), which was employing wet FGD at the time of WINTER. The use of wet FGD, therefore, is likely efficient at removing Br<sub>y</sub> from the flue gas prior to their release to the atmosphere.

The median emission ratio of Br<sub>y</sub>:SO<sub>2</sub> (where Br<sub>y</sub> = BrCl + BrNO<sub>2</sub> + 2×Br<sub>2</sub>) was \(1.5 \times 10^{-4}\) ppb:ppb (Figure 3), roughly 2 orders of magnitude lower than that of HCl:SO<sub>2</sub> (Figure 3). Though the native bromide to chloride content of coal is approximately 0.02, a dominant fraction of the bromine resulting from combustion should be made up of hydrogen bromide (HBr), as with its chlorine counterpart. However, three of the seven encounters in which Br<sub>y</sub> was observed exhibited observed levels that exceeded even the total reactive bromine (equation (2)) assuming all of the coal bromide was converted to Br<sub>y</sub> (plume encounters 5, 14, and 44), as shown in Figure S10b. Enhancements of Br<sub>y</sub> in plume encounters 5 (Figure S9) and 14 (Figure S11) were especially striking, considering that no significant enhancements in HCl, pCl, Cl<sub>2</sub>, or ClNO<sub>2</sub> were observed. This suggest either that (i) all of the bromide that was present in the coal was converted to Br<sub>y</sub>, BrNO<sub>2</sub>, and BrCl and that there was faster loss of Cl<sub>y</sub> relative to Br<sub>y</sub> during transport from source to observation point, which is unlikely, or (ii) the bromide to chloride ratio in the fuel was far greater than 0.02. As noted above, no facility reported adding bromide salts to its fuel. Plume encounters 5 and 44 occurred before sunset, which means that the Br<sub>y</sub> ratio to SO<sub>2</sub> was much greater at the source than downwind due to loss of Br<sub>y</sub> by photolysis.

A remaining question is whether Br<sub>2</sub>, BrNO<sub>2</sub>, and BrCl detected were directly emitted (i.e., following production in the flue gas by the reaction between mercury and bromine radicals; Jiao & Dibble, 2017) or produced following the emission of their potential precursors (i.e., HBr and/or pBr, neither of which was measured). The only known mechanism for efficient nighttime activation of halogens involve O<sub>3</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> (Simpson et al., 2015). However, the levels of N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub> at the center of the plumes were depleted relative to the levels outside of the exhaust, that is, were negatively correlated with SO<sub>2</sub> (Table 2), reflecting the elevated levels of NO which reacts rapidly with O<sub>3</sub> and NO<sub>3</sub>, the precursors to N<sub>2</sub>O<sub>5</sub>. Entrainment of O<sub>3</sub> at the edges could lead to N<sub>2</sub>O<sub>5</sub> production and chemistry but not in the plume core. When observed, all Br<sub>y</sub> species were strongly correlated with SO<sub>2</sub> throughout the plume. That is, they were not elevated only at the plume edges, as would be expected if chemical production occurred via N<sub>2</sub>O<sub>5</sub> or O<sub>3</sub> entrainment. This suggests direct emission of Br<sub>y</sub> or production by a reaction not involving known N<sub>2</sub>O<sub>5</sub>-driven chemistry.

### 4. Summary and Conclusions

We report on measurements of submicron pCl and pSO<sub>4</sub> and reactive gaseous halogen species including HCl, HOCl, Cl<sub>2</sub>, ClNO<sub>2</sub>, BrCl, Br<sub>2</sub>, and BrNO<sub>2</sub> observed in polluted air mass encounters during the WINTER campaign. A total of 50 plume encounters were identified, characterized by elevated SO<sub>2</sub> mixing ratios observed near and downwind of power plants, located in the northeast United States and also Georgia. Each of the 50 encounters was attributed to one or more operating power generation facilities using a simple wind trajectory approach. To our knowledge, this study represents the most comprehensive airborne assessment of halogen emissions from coal-fired power plants to date. HCl was typically the predominant chlorine-containing species in the 18 (out of 50) encounters with robust levels of HCl (~3 × LOD and \(R^2 \geq 0.4\) with...
The EPA role was limited to providing recommendation. U.S. EPA had no role in EPA approval, endorsement, or data interpretation. Mention of trade names, products, or environmental protection agency. Views or policies of the U.S. Environmental Protection Agency in this article are those of the authors and do not be interpreted as conveying, or one of their potential sources report using bromide salt additives during the time of WINTER. An accurate inventory of halogen emissions from coal-fired power plants, the second largest global source after sea spray, is crucial to assess the impact on regional oxidation and nitrogen cycling. These observations highlight the next challenge, which is to account for fuel composition and emission control technology on halogen emissions.

**References**


**Acknowledgments**

The authors acknowledge the NSF-NCAR Research Aircraft Facility engineers, scientists, pilots, and staff members. Funding for J. A. T. and L. J. was supported by the NSF AGS 1360745. J. C. S., P. C. J., and J. L. J. were supported by NSF AGS-1360834 and NASA NNX15AT96G. D. L. F. was supported by NSF 1433358. WINTER data are available on the NCAR website (http://data.eol.ucar.edu/master_list/?project=WINTER). The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Mention of trade names, products, or services does not convey, and should not be interpreted as conveying, official EPA approval, endorsement, or recommendation. U.S. EPA had no role in the collection or analysis of data. The EPA role was limited to providing publicly available information on power plants.