

An unexpected large continental source of reactive bromine and chlorine with significant impact on wintertime air quality

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Abstract

Halogen atoms affect the budget of ozone and the fate of pollutants such as hydrocarbons and mercury. Yet their sources and significances in polluted continental regions are poorly understood. Here we report the observation of unprecedented levels (averaging to hundreds of parts per trillion) of bromine chloride (BrCl) at a mid-latitude site in North China during winter. Widespread coal burning in rural households and a photo-assisted process were the main source of BrCl and other bromine gases. BrCl contributed about 55% of both bromine (Br) and chlorine (Cl) atoms. The halogen atoms increased the abundance of ‘conventional’ tropospheric oxidants (OH, HO₂, and RO₂) by 26-73%, and enhanced oxidation of hydrocarbon by nearly a factor of two and the net ozone production by 55%. Our study reveals the significant role of reactive halogen in winter atmospheric chemistry and in the deterioration of air quality in continental regions where uncontrolled coal combustion is prevalent.

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26

27 **ABSTRACT:**

28 Halogen atoms affect the budget of ozone and the fate of pollutants such as
29 hydrocarbons and mercury. Yet their sources and significances in polluted continental regions
30 are poorly understood. Here we report the observation of unprecedented levels (averaging to
31 60 parts per trillion) of bromine chloride (BrCl) at a mid-latitude site in North China during
32 winter. Widespread coal burning in rural households and a photo-assisted process were the
33 primary source of BrCl and other bromine gases. BrCl contributed about 55% of both bromine
34 (Br) and chlorine (Cl) atoms. The halogen atoms increased the abundance of 'conventional'
35 tropospheric oxidants (OH, HO₂, and RO₂) by 26-73%, and enhanced oxidation of hydrocarbon
36 by nearly a factor of two and the net ozone production by 55%. Our study reveals the significant

37 role of reactive halogen in winter atmospheric chemistry and the deterioration of air quality in
38 continental regions where uncontrolled coal combustion is prevalent.

39 **Keywords:** BrCl, reactive halogen, oxidation, coal burning, air pollution, northern China

40 41 **MAIN TEXT**

42 43 **Introduction**

44 Halogen atoms (Cl and Br) can strongly influence the atmospheric chemical
45 composition. High levels of halogens have been shown to deplete ozone in the stratosphere
46 [1] and destroy ground-level ozone of the Arctic [2-4]. There is an emerging recognition that in
47 the troposphere, they can kick start hydrocarbon oxidation that makes ozone, modify the
48 oxidative capacity by influencing the levels of OH and HO₂ radicals [5], perturb mercury
49 recycling by oxidizing elementary mercury (Hg⁰) to a highly toxic form (Hg^{II}) [4, 6]. Moreover,
50 Cl atoms can remove methane, a climate-forcing agent [7]. While most of the earlier halogen
51 studies focused on the stratosphere and the marine boundary layer, there has been growing
52 interest in the effect of Cl atoms on atmospheric chemistry over continental areas in the recent
53 decade because of the existence of anthropogenic chloride sources which can be activated to
54 form Cl atoms [8, 9]. Most of the previous studies focused on two Cl precursors, ClNO₂ and
55 Cl₂ [10-13], which were found to enhance ozone formation via Cl oxidation of hydrocarbons
56 [14-16]. However, our knowledge of the abundance and the role of bromine compounds in the
57 polluted continental troposphere is limited. During a recent winter field study in the North
58 China Plain (NCP), we observed surprisingly high levels of bromine chloride (BrCl), which
59 provides a significant source of Br and Cl atoms. We show that intense coal burning and
60 photochemical reactions are responsible for the observed BrCl and other reactive bromine
61 gases. Through model simulations, we reveal that BrCl and other halogens may alter ozone
62 production, hydrocarbon oxidation, and conversion of elemental mercury to a soluble form in
63 the surface layer of the atmosphere of the highly polluted NCP.

64 65 **Results and Discussions**

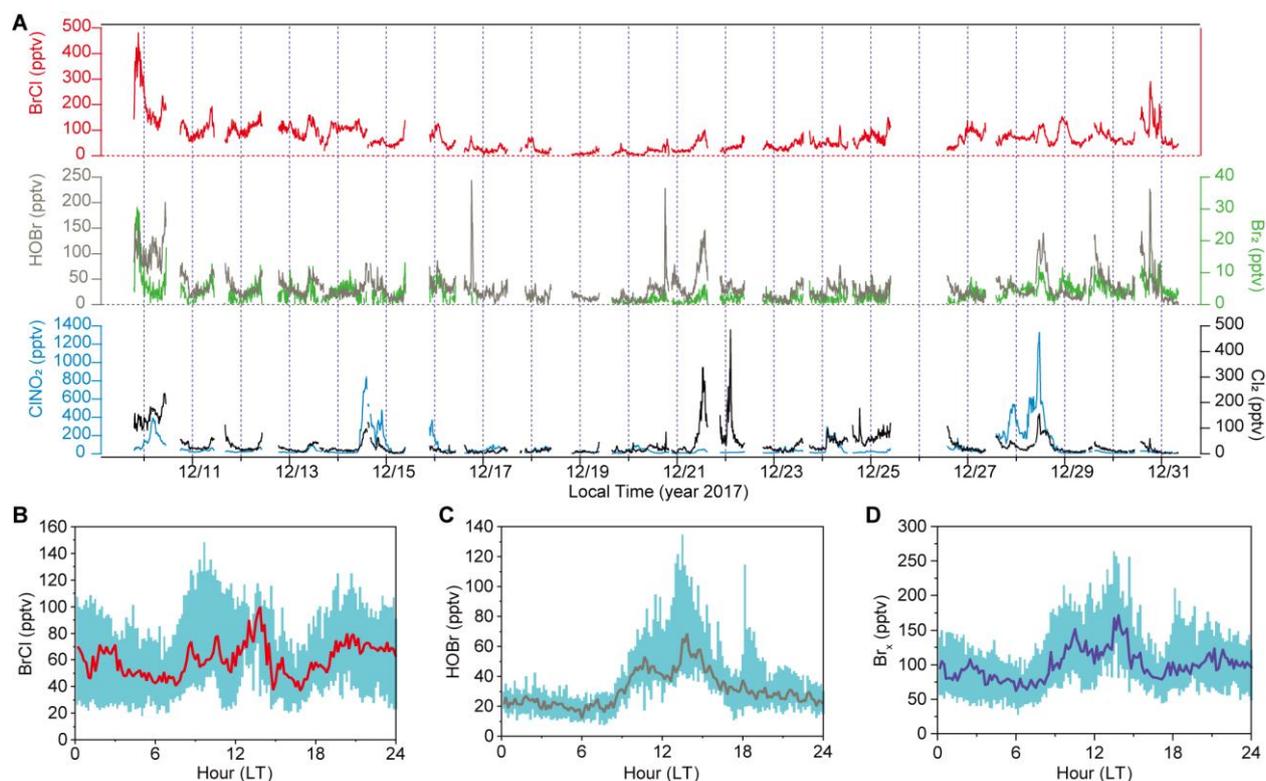
66 **Reactive halogen species observations**

67 Our measurements were conducted at the SRE-CAS station [17] in an agricultural field
68 in Hebei Province in the NCP during 9-31 December 2017 (Fig. S1A). The NCP is one of the
69 most populated regions in China and frequently suffers from severe haze pollution during
70 winters [18, 19] due to the high densities of human populations and industrial and agricultural
71 activities. Numerous villages in the NCP are within a few kilometers of each other (Fig. S1).
72 The measurement site is surrounded by villages with residents of ~ 1000, 1-2 km away from a
73 national highway (G4) and 3-4 km away from a provincial road (S335), and about 10 km
74 southeast of Wangdu township (Fig. S1). During the field measurement, the site was strongly
75 impacted by emissions from road traffic and rural household coal burning for heating and
76 cooking. As a result, extremely high levels of NO_x (83 ppbv on average) were observed with

77 elevated SO₂ (14 ppbv on average) and PM_{2.5} (137 μg/m³ on average). The O₃ concentrations
78 were low due to removal by high NO (53 ppbv on average) (Fig. S2).

79 Reactive halogen species (RHS), including BrCl, Cl₂, ClNO₂, Br₂, and HOBr, were
80 measured using a state-of-the-art chemical ionization mass spectrometry (CIMS) technique
81 (see Methods). To our knowledge, this is the first comprehensive measurement of RHS in
82 China. The data reveal three salient features. First, BrCl, a highly photolabile species,
83 frequently exceeded 100 pptv with a maximum value of 482 pptv (10-min average) (Fig. 1A).
84 The maximum value from our study is 10 times larger than the previously reported highest
85 value of 35 pptv in the Arctic [2]. It is also 5 times higher than the recent aircraft observed
86 BrCl (up to 80 pptv) in only one out of 50 coal-fired power plant plumes in the northeastern
87 US [20]. Apart from the latter study, BrCl had not been reported in field studies outside of the
88 polar regions [5]. Second, the average HOBr mixing ratio (34 pptv) is also one order of
89 magnitude larger than the level observed in the Arctic [21]. Third, BrCl and HOBr exhibited
90 higher concentrations in the daytime (8:00-16:00) (local time, LT), while considerable amounts
91 (~20 pptv) were still present at night (Fig. 1B, 1C). In terms of other RHS, ClNO₂
92 concentrations were lower than the previously observed values in the same area (but at a
93 different location) in the summer of 2014 [14], while the levels of Cl₂ (Fig. 1A) were
94 comparable to the summer values [16]. Br₂ was present at very low levels with an average
95 mixing ratio of 4 ppt, which was 3 times lower than a recently reported value in the Arctic [4]
96 (Fig. 1A). Additional information on the measurement site and ancillary measurements are
97 provided in the Supplementary Materials Section 2 and Section 3.

98



99

100 **Fig. 1. Ambient surface mixing ratios and diurnal profiles of reactive halogen gases at a**
101 **rural site in NCP during 9-31 December 2017. (A) Time series of Cl₂, ClNO₂, HOBr, Br₂,**

102 and BrCl. **(B)** The diurnal profiles of BrCl for the entire period. The red line is the median, and
103 the cyan shade represents the 25 percentile and 75 percentile values. **(C)** The diurnal profiles
104 of HOBr for the entire period. The brown line is the median, and the cyan shade represents the
105 25 percentile and 75 percentile values. **(D)** The diurnal profiles of gas-phase bromine Br_x (=
106 $\text{BrCl} + \text{HOBr} + 2 \times \text{Br}_2$) for the entire period. The purple line is the median, and the cyan shade
107 represents the 25 percentile and 75 percentile values.

110 **The source of reactive bromine species**

111 There is strong evidence that coal-burning was a major source of the measured reactive
112 bromine gases, Br_x , ($\text{Br}_x = \text{BrCl} + \text{HOBr} + 2 \times \text{Br}_2$). Br_x and two coal-burning tracers, sulfur
113 dioxide (SO_2) and selenium (Se) [22], were also elevated in the morning and early evening
114 (Fig. 2A), which is consistent with the increased coal use for heating and cooking during these
115 periods in rural homes according to our on-site survey in the village. Apart from emissions, the
116 concentrations of the measured chemical species would also affect the diurnal changes in the
117 planetary boundary layer height (PBLH), which was not measured during the study period. The
118 PBLH typically is at the maximum in the afternoon and reaches the minimum at night, which
119 means that surface emitted pollutants are expected to undergo more dilution during daytime
120 than at night. Therefore, the morning increase in mixing ratios of Br_x , the coal burning tracers,
121 and PBLH signify strong emission of local coal burning, whereas their later larger increase in
122 levels can be partly attributed to decreasing PBLH after sunset. Moreover, the Br_x showed a
123 good positive correlation with SO_2 (Fig. 2B; R^2 of 0.56 ± 0.17) and Se (Fig. S3A; R^2 of 0.58
124 ± 0.26) during the period of intensive coal burning (18:00-09:00) and when air masses were
125 relatively stable (wind speed < 3 m/s and no abrupt change in temperature and relative
126 humidity). In addition, particulate halides (chloride and bromide) exhibited the morning and
127 early evening peaks (Fig. 3, A and B) and also correlated with SO_2 and Se (Fig. S3, B and C)
128 throughout the campaign. Fig. S4A depicts a case of production of HOBr, BrCl, chloride, and
129 bromide in a fresh coal burning plume mixed with traffic emission (containing low O_3) in the
130 evening of 13 December. These results strongly indicate that coal-burning was a substantial
131 source of both reactive bromine gaseous (Br_x) and particle halides observed at our site.

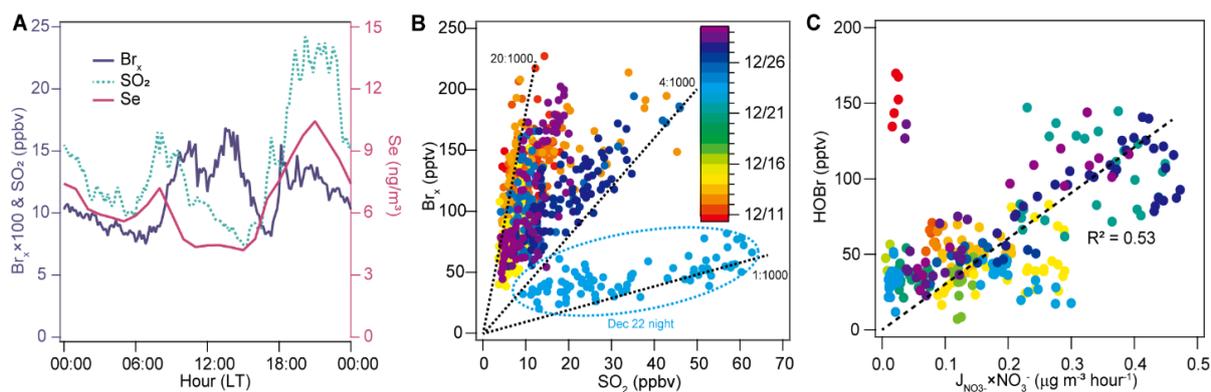
132 Fig. 2B and Fig. S3A indicate large variations in the observed ratios of Br_x to SO_2 or
133 Se, which can be explained by their relative content in coal, combustion conditions, and
134 atmospheric processing after emission. The unusual case on 22 December showed relatively
135 low levels of Br_x (~50 ppt) but very high loading of SO_2 (up to 80 ppb), resulting in the lowest
136 Br_x/SO_2 ratio (1:1000, mole/mole, see Fig. 2B). The very high concentrations of trace metal
137 elements (Mn and Fe) in this case (Fig. S5) reveal that the air mass might be strongly impacted
138 by emissions from coal burning and ore processing in steel industries. The lowest Br_x/SO_2
139 ratios may indicate a smaller emission of bromine relative to sulfur in iron-smelting processes,
140 incomplete activation of bromine in the air mass, or only partial accounting of reactive bromine
141 gases in the measured Br_x and more Br_x deposited relative to SO_2 in more aged air from the
142 steel factories (the nearest one is 80 km from the site). In comparison, the highest Br_x mixing
143 ratio was observed during the evening (19:00-24:00) on 9 December (Fig. 1A and Fig. S6) and
144 had a much larger Br_x/SO_2 ratio (13:1000, mole/mole), and this and most of the other cases

145 with moderate to high Br_x/SO_2 (4:1000-20:1000) in Fig. 2B could be characteristic of rural
146 coal-burning.

147 There are no reports on the concurrent Br_x and S measurements in domestic coal burned
148 effluent in China, and concurrently measured Br, Cl, and S content in Chinese coal. It is,
149 therefore, difficult to link our observed Br_x/S ratio to that ratio in coal. Nonetheless, we
150 compared the ambient molar $(\text{Br}_x + \text{Br}_{\text{particle}})/(\text{SO}_2 + \text{S}_{\text{particle}})$ and $(\text{Cl}_x + \text{Cl}_{\text{particle}})/(\text{SO}_2 + \text{S}_{\text{particle}})$
151 ratios with the average and range of Br/S [23, 24] and Cl/S [23, 25] ratios estimated from their
152 reported contents in Chinese coals (see Supplementary Materials Section 4). We found that the
153 ambient ratios were nearly one magnitude higher than the value of Br/S and Cl/S ratios in
154 Chinese coal, suggesting that halogen compounds are released in a much larger proportion
155 compared to sulfur, or that there are other sulfur species which are released during the
156 smoldering phase of coal burning but are not measured [26]. The Br_x/SO_2 ratios observed in
157 our study are one to two orders of magnitude higher than the ratio measured in the northeastern
158 US in the exhausts of coal-fired power plants that are not equipped with wet flue-gas
159 desulfurization [20]. This result indicates that large amounts of reactive bromine species could
160 be released from rural domestic coal burning in the NCP region. Based on the average content
161 of Br and Cl in 137 representative Chinese coal samples [23] and the annual coal assumption
162 in the NCP, we estimate that the amount of Br and Cl in coal can account for our observed
163 atmospheric values (see Supplementary Materials Section 5).

164 Another potential source of RHS is the open burning of crop residues, but they often
165 occurred in summer in the NCP [14]. We did observe high concentrations of particulate
166 potassium – a biomass burning tracer – on 26 December (Fig. S2), but the concurrent levels of
167 reactive halogen gases were not particularly high. Therefore, we propose that rural homes in
168 the NCP, mostly burning coal as the energy source in winter, is the source of reactive halogen
169 species in our study period. While we present strong evidence for coal-burning being a
170 significant source of the observed halogens, it is not clear whether BrCl and HOBr are directly
171 emitted or produced within the coal combustion plumes [20].

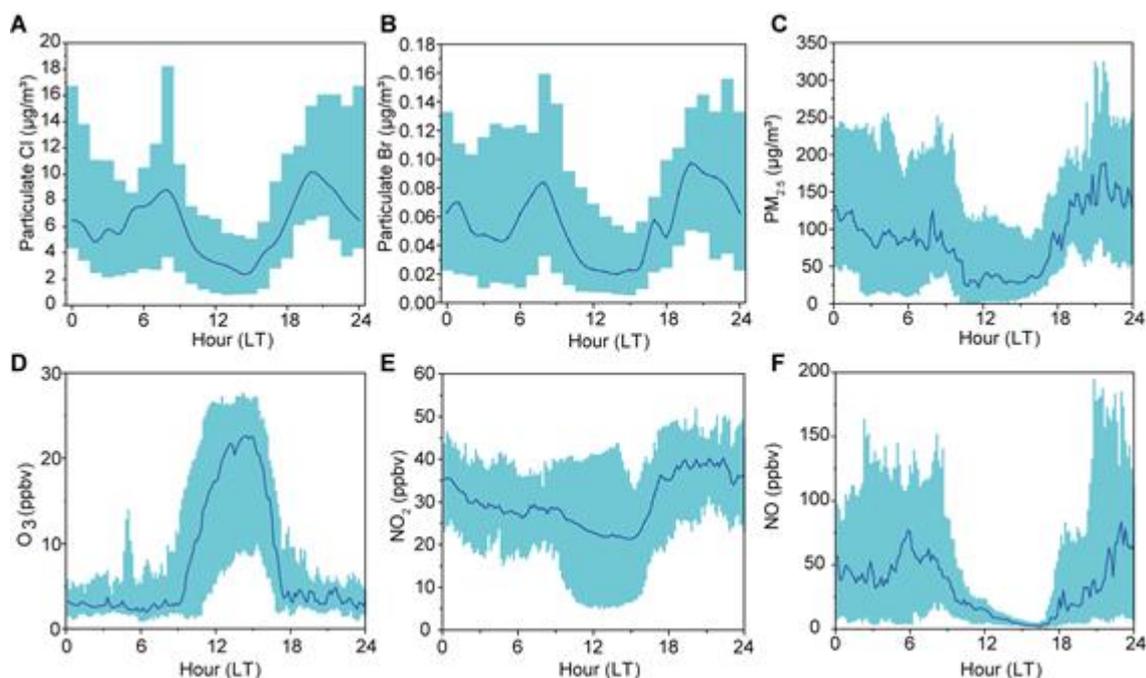
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174 **Fig. 2. Evidence for the source of the observed reactive bromine gases: coal burning and**
175 **photo-assisted activation process. (A)** Average diurnal profile of Br_x (purple line in 10-min
176 average), SO_2 (green dash line in 10-min average), and Se (red line in 1-hour average) during
177 9-31 December 2017. The lag in Br_x and its daytime peak are due to the photochemical release
178 of Br_x from particulate matter. **(B)** Scatter plot of 10-min average Br_x and SO_2 from 18:00 to

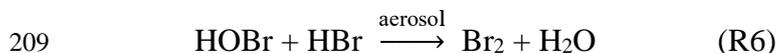
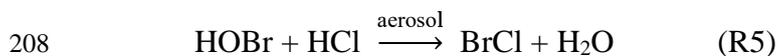
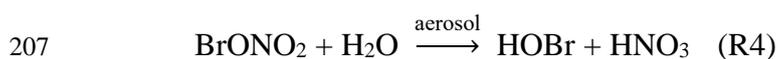
179 09:00 when the air masses were stable. Color coded according to sampling date on 9-31
 180 December 2017. ($\text{Br}_x = \text{BrCl} + \text{HOBr} + 2 \times \text{Br}_2$). The dotted lines indicate Br_x/SO_2 slope
 181 (mole/mole) of 1:1000 and 20:1000, which is the range of Br_x production from coal burning.
 182 Data in the oval depicts a case of industrial emissions. (C) Scatter plot of 10-min average HOBr
 183 and a proxy of photolysis rate of nitrate ($J_{\text{NO}_3^-} \times \text{NO}_3^-$ concentration) from 10:00 to 15:00. $J_{\text{NO}_3^-}$
 184 was calculated from the TUV model
 185 (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV) under clear sky conditions and
 186 then scaled to the measured J_{NO_2} . Color coded according to sampling date on 9-31 December
 187 2017. The outliers in the upper left corner are data from two days with the significant impact
 188 of fresh emissions or transport from the air aloft (Fig. S7).
 189



190
 191
 192 **Fig. 3. The observed diurnal profiles of trace gases and aerosol at the measurement site**
 193 **in NCP during 9-31 December 2017.** (A) particulate Cl, (B) particulate Br, (C) $\text{PM}_{2.5}$, (D)
 194 O_3 , (E) NO_2 , and (F) NO. The blue line is the median, and the cyan shade represents the 25
 195 percentile and 75 percentile values.
 196

197 Fig. 2A shows that the Br_x (and BrCl (Fig. 1B)) mixing ratios were highest in the
 198 afternoon and exhibited a larger fractional increase than SO_2 . Considering that BrCl is rapidly
 199 photolyzed (the noon-time photolytic lifetime of ~ 4 minutes) and the PBLH increases during
 200 the daytime, the increase in Br_x mixing ratio reveals a significant additional source facilitated
 201 by sunlight in order to sustain the observed Br_x levels during the daytime. The main
 202 photochemical chain cycle, which has been proposed to explain the elevated daytime Br_x in the
 203 Polar regions, involves R1-R8 [27].





212 The heterogeneous multi-step reaction of HOBr with chloride (R5) and with bromide
 213 (R6), which occurs on the surfaces of snow or sea-salt aerosols, is thought to be the primary
 214 source for the photolabile BrCl and Br₂, respectively [2, 5, 28-31]; additional pathways may
 215 also exist [5, 31]. In the daytime, Br atom from photolysis of Br₂ and BrCl initiates the above
 216 chain reactions to liberate more halogens (chlorine via R5 and bromine via R6) from the
 217 condensed phase, leading to a rapid increase in reactive bromine gases in the daytime
 218 (“bromine explosion”) [32].

219 In our study, the presence of elevated daytime BrCl and its good correlation with HOBr
 220 loss rate (Fig. S8) suggests that process R5 may play an important role at our site. Box model
 221 calculations using up-to-date gas-phase chemistry (see Supplementary Material Section 6) and
 222 a simplified halogen heterogeneous reaction scheme (see Supplementary Material Section 6.2)
 223 showed that R5 could account for a significant fraction of the observed BrCl when the model
 224 was constrained by the observed HOBr and other measurements (except BrCl). The observed
 225 low Br₂ concentrations indicate the lower importance of R6. The preponderance of R5 over R6
 226 at our site may be due to particulate chloride (7.3 μg/m³ on average) concentration being higher
 227 than bromide (0.07 μg/m³ on average). Because reaction R5 only activates particulate chloride
 228 (not bromide), the presently known bromine activation and propagation reactions (R1-R8)
 229 cannot explain the increasing Br_x concentrations in the daytime, and there should be an
 230 additional bromide activation process that produces HOBr or BrCl at our site. Previous
 231 laboratory studies [33-35] observed the production of Br₂ and BrCl when nitrate and halide in
 232 ice or snow are illuminated with ultra-violet light, and it was hypothesized that photolysis of
 233 nitrate aerosol generates OH radicals, which subsequently activate bromide to produce Br₂ and
 234 BrCl. During our study, we found a moderate correlation between HOBr and the proxy for
 235 aerosol nitrate photolysis rates (the product of calculated J_{NO3} and the measured PM_{2.5} nitrate
 236 concentrations) during 10:00-15:00 (R²=0.53) (Fig. 2C), which suggests that the photolysis of
 237 nitrate laden in particles may be involved in the activation of the bromide to produce HOBr
 238 (and further BrCl). The outliers in Fig. 2C are measurements taken on 29 December, when the
 239 sunlight intensity was very low and fresh coal burning plumes predominated (Fig. S7B), and
 240 also on 10 December, when downward transport from the residual layer was suggested by the
 241 increasing Br_x with decreasing other pollutants in the morning (Fig. S7A). Thus, these outliers
 242 did not reflect daytime chemistry. Given the considerable scattering in the data, we cannot
 243 exclude additional chemical or physical processes that may contribute to Br_x production. They
 244 include activation of bromide by an organic photosensitizer [36].

245

246 **Significant impact on atmospheric chemistry**

247 Given the high reactivity of Cl and Br atoms, we calculate the impact of the high BrCl
248 and other RHS (Cl₂, Br₂, HOBr, and ClNO₂) by using the aforementioned photochemical box
249 model that includes up-to-date Cl and Br gas-phase chemistry by constraining the model with
250 the measured RHS and other relevant observation data (see Supplementary Material Section
251 6.1). Because the measured RHS were constrained in the model, the simplified halogen
252 heterogeneous scheme was not used in the calculations of the halogen impact. Photolysis of
253 BrCl was the dominant source of the Cl atoms (~56%), which was 14 times higher than the
254 contribution from ClNO₂ and two times larger than that from Cl₂ (Fig. S9A). The model
255 predicted that Cl atoms reached a maximum concentration of about $\sim 9 \times 10^4 \text{ cm}^{-3}$ at noon (Fig.
256 4B), and the average concentration ($1.6 \times 10^4 \text{ cm}^{-3}$) is 26 times higher than the previously
257 modeled global mean level of 620 cm^{-3} [37]. The peak Cl production rate at our site ($\sim 8 \times 10^6$
258 $\text{cm}^{-3}\text{s}^{-1}$, Fig. S9A) is more than ten times that from photolysis of Cl₂ and ClNO₂ measured in
259 early winter at a ground site near the City of Manchester (UK) [12] and is several times the
260 primary Cl production rate from ClNO₂ (predominantly) and Cl₂ observed during an aircraft
261 campaign in the marine boundary layer off the coast of New York City (US) in late winter [13].
262 The BrCl was also the dominant source Br (~55%) at our site, followed by Br₂ (~20%) and BrO
263 (~13%) (Fig. S9B). The maximum Br production rate was $1.0 \times 10^7 \text{ cm}^{-3}\text{s}^{-1}$ (Fig. S9B), two
264 orders of magnitude larger than the maximum Br production rate predicted without
265 anthropogenic Br source in polluted coastal areas in the wintertime [38].

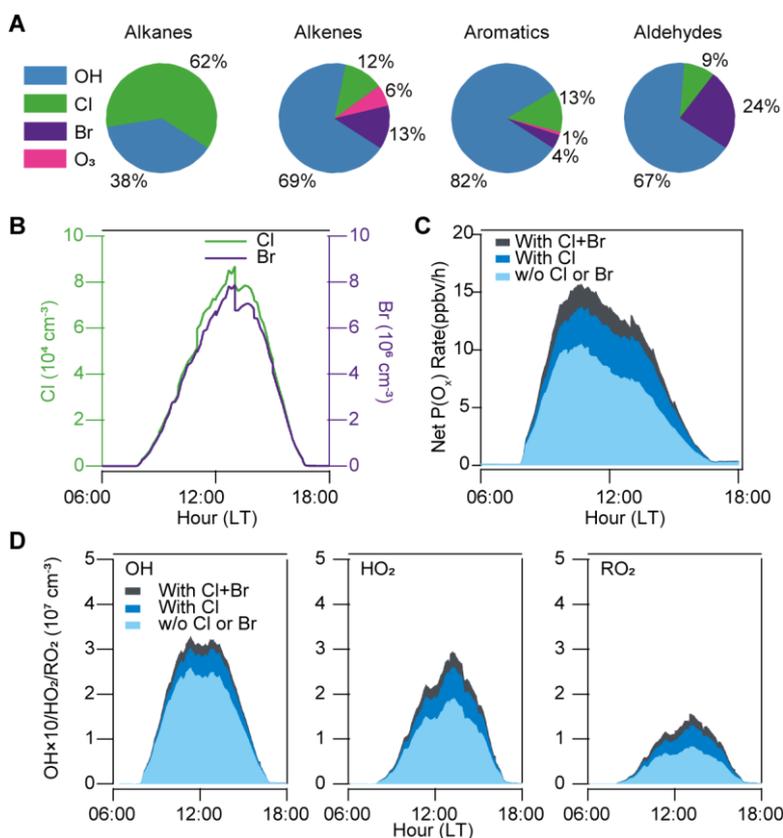
266 We find that the high levels of Cl and Br atoms have a profound impact on the oxidation
267 of VOCs. On average, ~60% of daily integrated oxidation of alkanes, ~10% of alkenes, ~15%
268 of aromatics, ~10% of aldehyde was oxidized by Cl atoms during daytime (Fig. 4A) at the
269 observation site. The Br atoms contributed up to ~15% of alkenes and ~25% of aldehydes
270 oxidation but negligibly to the alkanes and aromatics (Fig. 4A) since Br reactions with these
271 chemicals are very slow. The reactions of VOCs with Cl and Br atoms produce RO₂ radicals,
272 which are then recycled to form HO₂ and OH radicals, increasing the average concentration of
273 OH, HO₂, RO₂ oxidant radicals by ~25%, ~50%, and ~75%, respectively (Fig. 4D). These
274 results indicate that the abundance (and impact) of HO_x radicals (OH, HO₂, and RO₂) would
275 be significantly under-predicted if the halogen species found in our study are not considered.
276 A recent field measurement at a rural site north of Beijing in January 2016 [39] has shown
277 more than a factor of 1.5, 4, and 5 underpredictions of OH, HO₂, and RO₂ under high NO_x
278 conditions. The halogen (BrCl and Cl₂) induced chemistry could be part of the reason for the
279 under-estimation of HO_x.

280 When both direct (by halogen atoms) and indirect (from HO_x produced by the halogen
281 atom reactions) oxidation processes are included, the total VOCs oxidation rate increased by
282 ~180% for alkanes, ~50% for C₂-C₆ alkenes, ~40% for aromatics, and ~90% for aldehyde.
283 Moreover, the enhanced HO₂ and RO₂ increased O₃ production through reaction with NO. The
284 Cl and Br atoms enhanced the in-situ net chemical production rate of O_x (=O₃ + NO₂) (see
285 Supplementary Material Section 6.1) by 55% despite destroying ozone at the same time (Fig.
286 4C). Within these increases, Br atoms enhanced ~10% for OH, ~15% for HO₂, ~20% for RO₂,
287 and ~20% for net O_x production rate (Fig. 4, C and D). The result indicates that unlike the polar
288 and marine environments where hydrocarbons are low and lead to ozone destruction, the Br

289 atoms in the presence of large hydrocarbons can increase ozone production in polluted
 290 continental regions.

291 The halogen-initiated chemistry can also enhance secondary aerosol formation from
 292 oxidations of VOCs. The oxidation of VOCs by radicals leads to SOA formation via further
 293 reactions of RO₂ and OH to form low-volatility molecules [40]. Therefore, the halogen atoms,
 294 which have been shown to increase the RO₂ abundance by 75% on average, will significantly
 295 increase SOA production. In addition, the halogen enhanced HO_x can increase the production
 296 of other secondary aerosol observed during the haze events such as sulfate (by boosting SO₂
 297 oxidation with enhanced OH, O₃, and H₂O₂) and nitrate (via increasing NO_x oxidation by OH
 298 and O₃ to form nitric acid) [40]. Therefore, the inclusion of halogen sources discovered in our
 299 study in chemistry-transport models is likely to predict better the extent of winter haze
 300 formation in North China.

301



302

303 **Fig. 4. The model calculated contributions of hydrocarbons, ozone production rates, and**
 304 **radical abundance averaged for the entire period. (A)** Relative contribution to the daily
 305 integrated oxidation of alkanes, alkenes, aromatics, and aldehydes by OH, Cl, Br, and O₃. **(B)**
 306 The average diurnal profiles of Cl (green line) and Br (purple line) atom concentrations. **(C)**
 307 The average diurnal profiles of the net production rate of O_x (different color bars). The light
 308 blue bar, blue bar, and black bar represent results without Cl and Br chemistry, with only Cl
 309 chemistry, and with Cl and Br chemistry, respectively. **(D)** The average diurnal profiles of OH,
 310 HO₂, and RO₂ abundances. The light blue, blue, and black bars represent the same meaning as
 311 panel (C).

312

313 The large abundance of Br atoms can also significantly increase the conversion of
314 airborne elemental mercury (Hg^0) to reactive mercury (Hg^{II}). Hg^{II} is more soluble and hence
315 more prone to deposition to the surface than Hg^0 and is the main mercury species that deposits
316 and enter ecosystems [41]. Therefore, enhancing atmospheric oxidation would increase Hg^{II}
317 concentrations and deposition to the environment near the source. At our site, the atmospheric
318 lifetime of Hg^0 due to oxidation by OH or Cl is estimated to be longer than 70 days using the
319 reaction rate coefficients reported by Ariya et al. [42]. However, the lifetime is dramatically
320 shortened to only about 2 days when the average Br atom concentration of $1.5 \times 10^6 \text{ cm}^{-3}$
321 observed during the field study is used. These lifetimes are much shorter than the global
322 mercury lifetime of 10 to 13 months [41]. Given that coal burning also co-emits a large quantity
323 of mercury [43] and the NCP has one of the highest surface concentrations of Hg^0 in the world
324 [41], the fast bromine-induced Hg^{II} formation and subsequent deposition may significantly
325 increase the risk for human health and surface ecosystems in the NCP. Future studies are
326 needed to extend our near-field measurements and modeling impact of halogens to the other
327 parts of the boundary layer and downwind regions where coal-burning is common.

328

329 **Long-term and broad implications**

330 Although the above results are based on observations from one site, we suggest that
331 these findings apply to a large portion of China where coal burning is used to heat homes,
332 especially in the rural areas. In the year 2017, 17 million households in Hebei province use coal
333 as one of their energy sources. The Chinese government projects the four provinces (Hebei,
334 Shandong, Shanxi, and Henan) and two municipalities (Beijing and Tianjin) in the NCP to
335 account for 30% of China's total coal consumption in the year 2020 [44]. Therefore, BrCl is
336 expected to be ubiquitous over large areas of China with heavy coal burning, which is supported
337 by the observation of elevated levels of Br_x (up to 194 pptv) in March 2018 at the summit of
338 Mt. Tai, ~300 km south of the present site (Fig. S10).

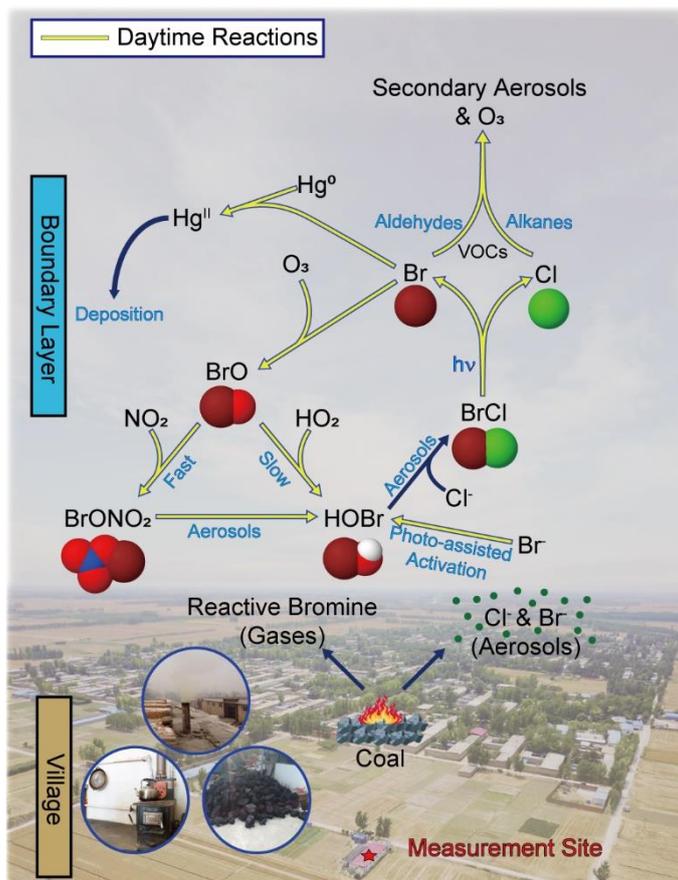
339 Recognizing a large contribution to air pollution by rural coal burning, the Chinese
340 government embarked on a massive campaign since the winter of 2018 to replace low-quality
341 coal with natural gas and electricity in rural areas of North China [45]. A recent report [46]
342 finds that while some progress has been made, mainly in regions surrounding Beijing, the
343 conversion campaign has been challenging in north-western (Shaanxi and Shanxi) and north-
344 eastern China (Heilongjiang) due to insufficient natural gas supply, inadequate electricity, and
345 the high costs of cleaner energy. Even within the NCP, the domestic coal burning in the
346 jurisdictions of Beijing, Tianjin, and 26 other cities still accounted for about 40% and 35% of
347 the total emission of SO_2 and $\text{PM}_{2.5}$ in the winter of 2019, with electricity and heat production
348 from coal-fired plants and other industrial coal-burning also contributing significantly [47].
349 The plunge in the air quality in the middle of February 2020 in the NCP despite drastic
350 reductions in traffic and some industrial activities amid the Coronavirus epidemic and the
351 Chinese New Year holiday [47] signified the persistence of coal-burning induced air pollution.
352 Therefore, coal burning will likely be a long-lasting and important source of winter air
353 pollution. Our study demonstrates that the intense coal burning not only emits large amounts

354 of primary pollutants such as particulate and sulphur [48, 49], but also promotes the formation
355 of secondary pollutants such as ozone, mercury (Hg^{II}), and organic aerosols by releasing highly
356 reactive halogen gases. The finding provides new scientific evidence to strengthen the impetus
357 to replace the use of dirty coal.

358 We note that as domestic coal burning is not limited to China, it is likely that similar
359 production of halogens occurs in other places where uncontrolled domestic coal-burning is
360 common. According to the International Energy Agency, coal production in 2017 accounts for
361 27.1% of the world's total energy supply [50], and the top 20 coal consuming
362 countries/economies are distributed over all inhabited continents (Table. S1). The dominant
363 use of coal in developed countries such as the United States, Japan, and Germany is for
364 electricity generation, where stringent pollution control measures are generally utilized.
365 However, a larger proportion of coal use for non-electricity production [50] and/or lower
366 implementation of pollution control in other countries/economies make coal burning as an
367 important source of air pollutants not only in China, but possibly also in India, Russia, and
368 South Africa, etc. Previous source apportionment of ambient $\text{PM}_{2.5}$ [51] and bottom-up
369 emission inventories [9] have indicated that coal burning is a major source of atmospheric
370 chloride, and field measurements in China and the US have observed elevated ClNO_2
371 associated air masses that were impacted by emissions of coal-fired power plants [10, 20, 52].
372 But only one study observed the presence of elevated BrCl in one, out of 50, plume from a
373 coal-burning plant in the US [20]. A better understanding of the sources, sinks, and impact of
374 reactive halogen species would enable quantification of the findings in the NCP in other
375 continental regions.

376 In summary, we have observed persistent and high concentrations of reactive bromine
377 species (BrCl and HOBr) at the ground level in a continental environment. As illustrated in
378 Fig. 5, the large reactive bromine species emerged from coal burning in rural households (and
379 industrial sources) and from daytime chemistry. Photolysis of BrCl significantly increased the
380 levels of Cl and Br atoms. These atoms, in turn, boosted the oxidation rates of VOCs and
381 mercury, and enhanced the abundance of HO_x radicals, leading to faster productions of
382 secondary pollutants such as ozone and organic aerosols. They also accelerated the deposition
383 of the toxic form of mercury. Our study reveals that anthropogenic reactive bromine may have
384 larger roles in the chemistry and air quality of the lower troposphere than previously thought,
385 and more research is warranted on the reactive halogen species, such as their source(s) and the
386 spatial extent of the role of the halogen chemistry, in the polluted continental atmosphere. Our
387 study also suggests the need to control halogens from coal-burning, in addition to CO_2 , sulfur,
388 nitrogen, PM , and mercury.

389



390

391 **Fig. 5. The simplified schematic representation of BrCl source and impact on**
 392 **tropospheric chemistry in North China.** Coal burning from rural households emits reactive
 393 bromine gases and particulate halogens in both daytime and nighttime. Daytime sunlight-
 394 assisted processes, possibly involving nitrate, activate particulate Br to produce HOBr and
 395 BrCl. BrCl is also produced by the reaction of HOBr with particulate Cl during day and night.
 396 BrCl is photolyzed to Cl and Br atoms in the daytime. VOCs are oxidized by Cl atoms (mainly
 397 on alkanes) and Br atoms (mainly on aldehydes) to produce ozone and secondary aerosols.
 398 Moreover, Br atoms significantly accelerate the mercury deposition near the source. All listed
 399 halogens are in the gas phase except for Cl⁻ and Br⁻. The three reactions (Br⁻ → HOBr, BrONO₂
 400 → HOBr, and HOBr → BrCl) are multiphase reactions, which can occur in/on condensed
 401 phase. The background photo shows the nearby village and the location of the measurement
 402 site. (Photo Credit: Chenglong Zhang and Pengfei Liu; RCEES, CAS).

403 METHODS

404 Field Measurements

405 Reactive halogen gases (RHS, including BrCl, HOBr, Br₂, Cl₂, ClNO₂), N₂O₅, other
406 trace gases (HONO, H₂O₂, SO₂, CO, NO, NO₂, and O₃), aerosol concentration and
407 compositions, particle size distributions, VOCs, OVOCs, JNO₂, and other meteorological
408 parameters were simultaneously measured in this study. In this section, we describe in detail
409 the RHS measurements and present information for other measurements in the supplementary
410 materials.

411 A quadrupole chemical ionization mass spectrometer (Q-CIMS) (THS Instruments
412 LLC, Atlanta GA.) was used to measure BrCl, HOBr, Br₂, Cl₂, ClNO₂, and N₂O₅ by using
413 Iodide (I⁻) reagent ions. The same instrument was used to measure N₂O₅ and ClNO₂ in our
414 previous studies [14, 15]. In this study, each target species was monitored at more than two
415 isotopic masses to ensure accurate identifications of ion clusters. BrCl was monitored at 241
416 amu (I⁷⁹Br³⁵Cl⁻), 243 amu (I⁷⁹Br³⁷Cl⁻; I⁸¹Br³⁵Cl⁻), and 245 amu (I⁸¹Br³⁷Cl⁻). HOBr was
417 monitored at 223 amu (IHO⁷⁹Br⁻) and 225 amu (IHO⁸¹Br⁻). Br₂ was monitored at 287 amu
418 (I⁷⁹Br⁸¹Br⁻) and 289 amu (I⁸¹Br⁸¹Br⁻). Cl₂ was monitored at 197 amu (I³⁵Cl³⁵Cl⁻) and 199 amu
419 (I³⁵Cl³⁷Cl⁻). ClNO₂ was monitored at 208 amu (I³⁵ClNO₂⁻) and 210 amu (I³⁷ClNO₂⁻). The BrO
420 results are not shown here as we found the BrO measurement suffered mass spectral
421 interference as indicated by the very weak correlation of the observed masses at 222 amu and
422 224 amu. Hourly scans of the mass spectrum showed that the signal strength for BrNO₂ (252
423 amu, 254 amu) was below the CIMS's detection limit.

424 The CIMS instrument was housed in a single-story shelter. The sample line was a total
425 3.5 m long PFA-Teflon tubing (1/4 in. outer diameter), with the sampling inlet approximately
426 1.5 m above the rooftop. We tried to minimize potential inlet artifacts by (1) configuring the
427 sampling inlet system (Fig. S11) to divert large particles from the sample inlet into a by-pass
428 flow and reducing the residence time of the measured gases below 0.5 seconds; and (2)
429 changing and washing the entire sampling inlet every day to reduce the deposition of Cl⁻ and
430 Br⁻ containing particles on the inlet wall. There were no noticeable changes in the HOBr and
431 BrCl signals when the tubing was replaced (Fig. S4, B and C), strongly suggesting the absence
432 of significant heterogeneous reactions in the sample line after using the inlet for a day.

433 The instrument background signal was measured every day by scrubbing ambient air
434 with alkaline glass wool and charcoal, as many inorganic halogens are efficiently removed by
435 this process, which has also been used by other groups for halogen measurements [3, 16, 53].
436 The instrument sensitivity for Cl₂ and ClNO₂ was determined on-site every two days. A Cl₂
437 permeation tube was used as the calibration source, and its permeation rate (378 ng/min,
438 variation <5%) was determined before and after the campaign. The sensitivity of Cl₂ was stable
439 (2.0±0.16 Hz/pptv) (Fig. S12A) with no significant dependence on RH (Fig. S12B). The
440 uncertainty for the Cl₂ measurement was about 25%. The calibration method of ClNO₂ has
441 been reported in our previous studies [14, 15]. The sensitivities for other halogen species (Br₂,
442 HOBr, and BrCl) were determined according to their sensitivity ratio relative to Cl₂, which was
443 determined after the field study. The calibration of Br₂ was similar to Cl₂, which was achieved
444 by a permeation tube standard. The HOBr was calibrated using the same method described by
445 Liao et al. [3]. HOBr was synthesized from the reaction of liquid Br₂ with a 0.1 M silver nitrate
446 solution (AgNO₃), and its concentration was calculated from the Br₂ formation by passing the

447 HOBr standard through sodium bromide slurry (NaBr). The calibration of BrCl was achieved
448 using the method described by Neuman et al. [54], which was also used by Liao et al. [3] and
449 Le Breton et al. [55]. Briefly, the Br₂ and Cl₂ permeation tubes were placed in the same oven
450 at 40 °C to produce BrCl via reaction of Cl₂+Br₂→2BrCl. We have confirmed in the laboratory
451 that all reduction of Br₂ and Cl₂ were converted into BrCl. The concentration of BrCl was
452 calculated from the reduction of Br₂. The sensitivity of Br₂, BrCl, and HOBr was 1.4 Hz/pptv,
453 1.6 Hz/pptv, and 2.1 Hz/pptv, respectively. The measurement uncertainty for Br₂, BrCl, and
454 HOBr was about 25%, 35%, and 39%, respectively.

455 To make sure no significant spectral interference for signals of BrCl, HOBr, and Cl₂,
456 we checked their isotopic signals that showed a strong correlation with slopes being close to
457 the respective theoretical isotopic ratio (Fig.S13). Potential artifacts from the inlet or
458 instrument are of critical concern. We have scrutinized all key steps in our CIMS measurements
459 and made sure that the HOBr and BrCl measurements did not suffer significant artifacts. We
460 examined and ruled out five potential artifacts in the inlet or instrument: (i) Inlet artifacts from
461 O₃ heterogeneous reactions, (ii) Potential secondary ion chemistry with IO₃⁻ in the ion chamber.
462 (iii) Secondary ion chemistry with IH₂O⁻ in the ion chamber. (iv) Mass spectral influence from
463 SO₂. (v) Inlet artifacts for BrCl measurement from further HOBr reactions. The detailed results
464 are provided in the Supplementary Material Section 1. In short, we did not find evidence of
465 significant interference or artifacts which would undermine our halogen measurements.

466

467 **Chemical Box Model**

468 An zero-dimensional chemical box model was built based on the latest version of the
469 Master Chemical Mechanism v3.3.1 by using the Kinetic Pre-Processor (KPP) [56] on a
470 MATLAB platform. To better represent the halogen chemistry, we modified the mechanisms
471 to include chlorine and bromine related reactions. The detailed kinetics data adopted in the
472 model are listed in Table S2 and described in the supplementary materials. In this study, we
473 used the model to calculate the impact of Cl and Br atoms on oxidation chemistry (see
474 Supplementary Material Section 6.1). The model was constrained to observations of RHS
475 (BrCl, HOBr, Br₂, Cl₂, ClNO₂), N₂O₅, HONO, O₃, H₂O₂, NO, NO₂, SO₂, CO, temperature,
476 aerosol surface area density, J_{NO2}, VOCs, and OVOCs. Table S4 shows a summary of the input
477 parameters in the model. Other detailed information on photolysis frequencies, dry deposition,
478 the boundary layer height, the wet deposition is described in the supplementary materials. We
479 also combined it with a simplified halogen heterogeneous reaction scheme to estimate the BrCl
480 production (see Supplementary Material Section 6.2).

481

482

483

484 **SUPPLEMENTARY MATERIALS**

485 Supplementary materials are available online, which includes:

486 Section S1. CIMS Measurement

487 Section S2. Measurement Site

488 Section S3. Other Measurement Instruments Used in the Work

489 Section S4. Comparison of Ratios of Halogen to Sulfur in Ambient Air and Coals

490 Section S5. Accounting for Observed Halogens

491 Section S6. Chemical Box Model

492 Supplementary Figures: Figure S1 to S15
493 Supplementary Tables: Tables S1 to S5
494 References

495

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501

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512

513 **AUTHOR CONTRIBUTIONS**

514 T.W. designed halogen research. J.C. and Y.M. planned and organized the overall field
515 campaign at Wangdu. X.P., M.X. and W.W. conducted measurements of the halogen species
516 by CIMS. X.P. and W.W. set up the halogen calibration method, built the chemical box model,
517 and performed laboratory tests. Q.L. helped model development. L.X. helped the box model
518 development and validation. P.L., C.Z. performed measurements of SO₂, NO_x, O₃, HONO, and
519 H₂O₂. H.C., F.Z., C.Z., and J.W. performed VOCs and OVOCs measurements. H.C., P.L., and
520 F.Z. performed particulate matter measurements (elementary analyzer, ACSM, OC, EC, WSI
521 in the offline filter). M.X. and X.W. performed JNO₂ measurements. H.C. and F.Z. performed
522 aerosol size distribution measurements. X.P., W.W., T.W., and A.R.R. analyzed the data and
523 interpreted the results, with contributions from A.S-L, Q.L., C.G., and Y.M.. T.W., X.P., and
524 W.W. wrote the paper, with significant input from A.R.R., A.S-L., and H.C. All authors
525 reviewed and commented on the paper.

526

527 **COMPETING INTERESTS DECLARATION**

528 None declared.

529

530

531 **DATA AVAILABILITY**

532 All data needed to evaluate the conclusions in the paper are present in the paper and/or the
533 Supplementary Materials. CIMS measurement data is available by contacting the
534 corresponding author (T.W.) (cetwang@polyu.edu.hk). Other data is available by contacting
535 J.C. (jmchen@fudan.edu.cn) and Y.M. (yjmu@rcees.ac.cn).

536

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