Correction

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Correction for "Airborne measurements of organic bromine compounds in the Pacific tropical tropopause layer," by Maria A. Navarro, Elliot L. Atlas, Alfonso Saiz-Lopez, Xavier Rodriguez-Lloveras, Douglas E. Kinnison, Jean-Francois Lamarque, Simone Tilmes, Michal Filus, Neil R. P. Harris, Elena Meneguz, Matthew J. Ashfold, Alistair J. Manning, Carlos A. Cuevas, Sue M. Schauffler, and Valeria Donets, which appeared in issue 45, November 10, 2015, of *Proc Natl Acad Sci USA* (112:13789–13793; first published October 26, 2015; 10.1073/pnas.1511463112).

The authors note that, due to a printer's error, in the Abstract, lines 12–13, and on page 13789, right column, second full paragraph, line 12, "parts per thousand" should instead appear as "parts per trillion."

CORRECTION

Airborne measurements of organic bromine compounds in the Pacific tropical tropopause layer

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Very short-lived brominated substances (VSLBr) are an important source of stratospheric bromine, an effective ozone destruction catalyst. However, the accurate estimation of the organic and inorganic partitioning of bromine and the input to the stratosphere remains uncertain. Here, we report near-tropopause measurements of organic brominated substances found over the tropical Pacific during the NASA Airborne Tropical Tropopause Experiment campaigns. We combine aircraft observations and a chemistry–climate model to quantify the total bromine loading injected to the stratosphere. Surprisingly, despite differences in vertical transport between the Eastern and Western Pacific, VSLBr (organic + inorganic) contribute approximately similar amounts of bromine [~6 (4–9) parts per thousand] to the stratospheric input at the tropical tropopause. These levels of bromine cause substantial ozone depletion in the lower stratosphere, and any increases in future abundances (e.g., as a result of aquaculture) will lead to larger depletions.

bromine | ATTREX | tropopause

Until the end of the last century, it was believed that only long-lived species, like bromomethane (CH_3Br) and halons, contributed to the global burden of stratospheric bromine. However, disagreement between the observed amount of reactive stratospheric bromine and the sources of long-lived trace gases suggested the existence of an additional contributor: Very short-lived brominated substances (VSL_{org}) [VSL_{org} = bromoform ($3CHBr_3$) + dibromomethane ($2CH_2Br_2$) + $minor_{VSLBr}$, where $minor_{VSLBr}$ = bromochloromethane (CH_2BrCl) + dibromochloromethane ($2CHBr_2Cl$) + bromodichloromethane ($CHBrCl_2$)] that originate mainly from ocean biogenic sources (1, 2).

Several studies have described the processes involved in the transformation of biogenic bromocarbons to inorganic bromine, and their transport through the tropical tropopause layer (TTL) (1–5). These studies have led to significant progress in modeling the VSL_{org} contribution to the formation of stratospheric inorganic bromine (Br_y) (3, 4, 6–11). However, the scarcity of observations to constrain the emissions, the impact of deep convection, and the effect of dehydration processes limit the prediction of short-lived source gases that reach the stratosphere (3). On the other hand, atmospheric observations of VSL_{org} have been provided by ground measurements and cruise, balloon, and airborne campaigns (12–14), but the different instruments used between campaigns, and the low spatial and temporal coverage of each study, contribute to the uncertainties in the estimations of total bromine and its partitioning (15). In an attempt to reduce these limitations, we present unique measurements of organic bromine substances carried out with the same instrument, the Global Hawk Whole Air Sampler (GWAS), deployed during the NASA Airborne Tropical Tropopause Experiment (ATTREX), which covered the tropical Pacific region during 2013 and 2014 (see *SI Text* for details of the campaign).

Because coastal areas of tropical waters (like the Maritime Continent) are an important source for VSL_{org} (16–18) and highly convective zones can transport air masses from the troposphere into the stratosphere through the TTL (19), we focus this study on observations taken over the Western Pacific (120°E–165°E) and the Eastern Pacific (187°E–268°E) (Fig. S1). We compared these regions in terms of VSL_{org} mixing ratios at the tropopause level (~17 km; Fig. S2), which defines the chemical composition of air that enters the stratosphere.

Whole air samples were collected during two deployments of the ATTREX campaigns, on board the unmanned aerial vehicle Global Hawk. Measurements of VSL_{org} were carried out in the field using a combination of gas chromatography with mass selective, flame ionization, and electron capture detectors (*Materials and Methods*). Fig. 1 *A* and *B* displays the observations of $CHBr_3$, CH_2Br_2, and $minor_{VSLBr}$, as well as the total organic bromine mixing ratio, in the upper troposphere/lower stratosphere (UTLS) of the Western and Eastern Pacific. GWAS observations indicate that the total amount of VSL_{org} that enters the stratosphere over the Western and Eastern Pacific is approximately similar, 3.27 ± 0.47 parts per thousand (ppt) and 2.96 ± 0.42 ppt, respectively. These observations are compared with the state-of-the-art Community Atmosphere Model (CAM-Chem) simulations (4, 20) (see *Materials and Methods*). The results show good agreement with the measurements, and simulate the injection of VSL_{org} to the stratosphere of 3.84 ± 0.64 ppt and 3.18 ± 1.49 ppt

A Western Pacific **B Eastern Pacific**

- VSL$_{org}$ ▲ CHBr$_3$
- CH$_2$Br$_2$ ▼ Minor VSL$_{org}$
- Br$_y$

(A, B) plots:
(3.84 ± 0.64) ppt GWAS= 3.27 ± 0.47 ppt
(3.18 ± 1.49) ppt GWAS= 2.96 ± 0.42 ppt

(C, D) plots:
1.97 ± 0.21 ppt
3.02 ± 1.90 ppt

Altitude (km) — axis values 14, 15, 16, 17, 18

Mixing ratio (ppt) — axis values 0 1 2 3 4 5 6 7 8 9 10

Fig. 1. GWAS measurements and CAM-Chem simulations ±1 SD. Filled symbols are the 1 km average bins from GWAS measurements. Lines are the CAM-Chem simulation. Values from the arrows represent the mean mixing ratio (ppt) of VSL$_{org}$ and Br$_y$ at the tropopause level (∼17 km) derived from CAM-Chem simulations. (A and B) Organic brominated species multiplied by their atomicity for (A) Western Pacific and (B) Eastern Pacific. (C and D) CAM-Chem estimations of inorganic bromine (Br$_y$) from measured brominated VSLS with shaded ±1 SD for (C) Western Pacific and (D) Eastern Pacific.

organic Br for the Western and Eastern Pacific, respectively (Fig. 1 A and B).

Although negligible differences of the organic fraction of VSLBr were observed between the Western and Eastern Pacific, we quantified the inorganic fraction coming from the degradation of VSL$_{org}$. Estimations of inorganic bromine (Br$_y$ = Br + BrO + HOBr + BrONO$_2$ + HBr + BrCl + 2Br$_2$ + BrNO$_2$ + IBr), with a focus at ∼17 km, were calculated with the CAM-Chem model using assimilated meteorological fields for each Global Hawk flight. According to these simulations, the amount of Br$_y$ over the Eastern Pacific is 3.02 ± 1.90 ppt, whereas, in the Western Pacific, the mixing ratio of Br$_y$ is 1.97 ± 0.21 ppt (Fig. 1 C and D). Br$_y$/VSL$_{org}$ ratios show that at ∼17 km, the abundance of Br$_y$ over the Western Pacific is almost half the amount of VSL$_{org}$, in contrast to the Eastern Pacific, where the abundance of Br$_y$ is similar to the value of VSL$_{org}$ (Table 1).

We evaluated these different Br$_y$/VSL$_{org}$ ratios with 12-d back-trajectory analyses using the Numerical Atmospheric dispersion Modeling Environment (NAME) (21) (see *Materials and Methods*). These analyses indicate that a variety of source regions influenced our samples in the TTL during the ATTREX flights (see *SI Text* for details). However, the majority of air transported to the tropopause region (∼17 km) of the Eastern and Western Pacific last encountered the boundary layer in the area between 90°E and −140°E (Fig. S3). Fig. 2 A and B shows two representative cases of the locations where the back-trajectories first crossed the 1-km-altitude surface for samples collected over the Western and Eastern Pacific, respectively. This similarity on the source location of the air mass could explain the similar amount of VSL$_{org}$ observed over both the Western and Eastern Pacific.

The NAME analysis indicates that the mean time for the boundary layer (<1 km) air to reach the air sampled at 17 km was 9.8 d in the West Pacific samples and 11.1 d in the East Pacific. This difference in mean times, along with the difference between East and West Pacific in the fraction of trajectories that reach 1 km, is consistent with the observed differences in the mixing ratios of the shorter-lived gases such as methyl iodide, bromoform, and propane (Table S1). Our analysis suggests that the air encountered around the tropopause was composed of two well-mixed fractions: a "young" one, containing fresh emissions transported recently from the boundary layer and low troposphere within the previous days, and an "aged" fraction, which had been in the TTL for weeks to months (e.g., Fig. 2C and Fig. S4D). This is supported by 30-d back-trajectories calculated by NAME, which show that the influence of convective events between days 12 and 30 was small. The same analyses show that differences of Br$_y$ could be due to transport dynamics, mixing processes, and age of air masses targeted during the field campaigns. Flights over the Western Pacific tracked fresh air from the air masses detrained into the TTL by Tropical Storm Faxai and air from the South Pacific Convection Zone. Thus, most of the air masses that reached ∼17 km during these two events moved from the boundary layer to the upper troposphere (UT) rather than following the horizontal pattern seen on most of the air masses tracked over the Eastern Pacific (Fig. 2 C and D). We suggest that these "fresh" air masses, quickly transported to the UT, limit the chemistry that leads to the formation of Br$_y$, and reduce their abundance over the Western Pacific. From another point of view, the higher stratospheric injection of Br over the Eastern Pacific could be also related to transport time and distance. For example, as the air masses travel from West to East, heterogeneous recycling reactions could put more Br back into the troposphere than washout is removing. Previous studies have pointed out that rapid uplift of air masses, due to convection events, as well as the colder temperatures within the TTL, can considerably enhance the efficiency of heterogeneous reactions relative to complete washout or ice removal (3, 4, 22, 23). However, the impact of heterogeneous reactions depends on several factors, including the microphysical environment and the partitioning of the inorganic bromine species. Hence, further analysis of the Br$_y$ chemical speciation over the Eastern and Western Pacific could provide insight into these fundamental processes.

Based on the CAM-Chem simulation results, the overall contribution of VSL substances (VSL$_{org}$ + Br$_y$) to total stratospheric bromine, quantified at ∼17 km, show 5.81 (5.14–6.48) ppt over the Western Pacific and 6.20 (3.79–8.61) ppt over the Eastern Pacific (Table 1).These results point out that although the production of Br$_y$ seems to be slightly different between the Eastern and Western Pacific (within ±1 std dev), the overall contribution of

Table 1. Organic and inorganic ratio of bromine over the Western and Eastern Pacific Ocean at ∼17 km and total VSLBr contributions

Values at 17 km	Western Pacific	Eastern Pacific
From CAM-Chem		
VSL$_{org}$, ppt	3.84 ± 0.64	3.18 ± 1.49
Br$_y$, ppt	1.97 ± 0.21	3.02 ± 1.90
Br$_y$/VSL$_{org}$	0.51 ± 0.04	0.95 ± 0.32
VSLBr (Br$_y$ + VSL$_{org}$),* ppt	5.81 ± 0.67	6.20 ± 2.41
From GWAS		
VSL$_{org}$, ppt	3.27 ± 0.47	2.96 ± 0.42
VSLBr (Br$_y$ + VSL$_{org}$),† ppt	5.24 ± 0.51	5.98 ± 1.95

*VSLBr from CAM-Chem. Both VSL$_{org}$ and Br$_y$ are estimates from CAM-Chem model.
†VSLBr from GWAS. VSL$_{org}$ are the measurements from GWAS, and Br$_y$ are estimates from CAM-Chem model.
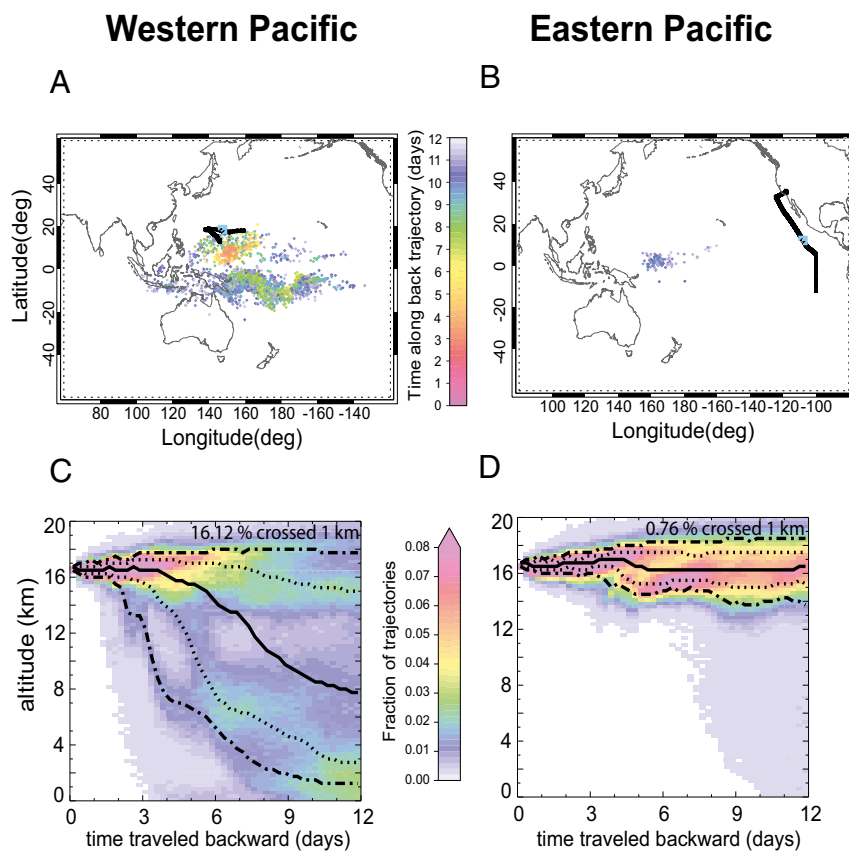
Western Pacific　　　Eastern Pacific

Fig. 2. NAME 12-d back-trajectories for samples collected over the Western Pacific (*A* and *C*) on 4 March 2014 (at 16.58 km, 18.341°N, 147.494°E), and over the Eastern Pacific (*B* and *D*) on 22 February 2013 (at 16.54 km, 12.007 °N, 107.82°W). (*A* and *B*) Location at which trajectories first crossed 1 km, with the color indicating the time taken to reach this altitude. Black line indicates the ATTREX flight path. Light blue mark represents the location of the GWAS sample where the trajectories start. (*C* and *D*) Probability distribution of trajectory altitude as a function of time traveled backward. The median trajectory altitude is marked with a solid line, 25th and 75th percentiles are marked with dotted lines, and 10th and 90th percentiles are marked with dot–dash lines.

very short-lived substances to stratospheric bromine is similar in both regions. The average value of the two subsets of ATTREX mission [~6 (4−9) ppt] agrees with the current estimate proposed by the World Meteorological Organization (WMO) [~5 (2−8) ppt], which is based on measured VSL source gas concentrations (24). Note that this estimate based on model results is slightly higher and has a slightly narrower range than the 2014 WMO O_3 assessment. However, using the same methodology as the 2014 WMO O_3 assessment, GWAS measurements show that the contribution of VSL substances to total stratospheric bromine would be slightly lower [i.e., 5.24 (4.73–5.75) ppt over the Western Pacific and 5.98 (4.03–7.93) ppt over the Eastern Pacific (Table 1)]. There are still some fundamental uncertainties in characterizing the overall contribution of VSL substances to total stratospheric bromine, as essentially all of the inorganic bromine information described here comes from model calculations.

The impact of the VSL_{org} on the composition of the tropopause region is also observed in the total organic bromine budget. The vertical distribution of VSL_{org} along with halons (Halon 1211+ Halon 2402) and CH_3Br, also measured in the field, was examined here (Fig. S5 *A* and *B*). Halon 1301 was not measured during ATTREX, and its contribution to the Br budget was estimated from measurements at surface sites (25). Remarkably, the results show similar profiles in the UTLS, and relatively little variation, between the Eastern and Western Pacific. In addition, CAM-Chem model simulations clearly capture the distribution and variability of these three major groups. The total organic bromine budgets at the tropopause (17 km, $\theta \approx 370$ K) resulted in 18.02 ± 0.66 ppt and 17.68 ± 0.49 ppt in the Western and Eastern Pacific, respectively (Table 2). These values are similar to the total organic bromine of 17.4 ± 0.9 ppt reported over the Central Pacific during NASA-Stratospheric Tracers of Atmospheric Transport (NASA-STRAT) 1996 (26, 27) and to the total

Table 2. Total Organic Bromine Budget at 17 km from ATTREX and two other missions over the Eastern and Western Pacific

Campaign location	STRAT 1996* Central Pacific, ppt (%)	CRAVE 2006 Eastern Pacific, ppt (%)	ATTREX 2013–2014 Western Pacific, ppt (%)	Eastern Pacific, ppt (%)
Halons	6.63 ± 0.22 (38)	8.26 ± 0.09 (47)	7.59 ± 0.19 (42)	7.92 ± 0.11 (45)
CH_3Br	9.45 ± 0.39 (54)	7.83 ± 0.16 (45)	7.16 ± 0.41 (40)	6.80 ± 0.23 (38)
VSL_{org}	1.30 ± 0.40 (7)	1.42 ± 0.52 (8)	3.27 ± 0.49 (18)	2.96 ± 0.42 (17)
Total organic bromine budget	17.4 ± 0.9	17.5 ± 0.6	18.02 ± 0.66	17.68 ± 0.49

*Values calculated from data presented in tables and text in Schauffler et al. (26, 27).

organic bromine of 17.5 ± 0.6 ppt found over the Eastern Pacific during NASA-Costa Rica-Aura Validation Experiment (NASA-CRAVE) 2006 (https://espoarchive.nasa.gov/archive/browse/cr_ave). The similarity between campaigns over this extended time period reflects the changing abundances of the long-lived species (bromomethane and halons) and the variable amounts of short-lived bromine compounds found during the few campaigns that have collected data in the tropical TTL (25, 28, 29). During the time period from 1996 until 2014, methyl bromide has been declining globally (28). The global average of CH_3Br has been reduced by ~3.5 parts per trillion volume (pptv) during this time. At the same time, the total amount of halons has seen an increasing trend that reached a broad maximum during 2004–2008, and has slowly declined since then. For the missions shown in Table 2, the global average mixing ratio of halons (measured at the surface) changed from 7.19 pptv during STRAT to 8.32 pptv during CRAVE, then to 7.97 pptv and 7.85 pptv during the 2013 and 2014 ATTREX campaigns, respectively. The measurements of long-lived organic Br compounds in the TTL region shown in Table 2 show a good correspondence to the trend determined from surface sites. The overall decrease in long-lived organic bromine amounts to ~1.8 pptv from 1996 to 2014. The drop in bromine due to the long-lived bromine species is masked by the increasing amount of organic bromine from VSLS that was observed during ATTREX compared with the earlier campaigns. Because of the expected variability of the VSLBr and the effect of different meteorological and sampling conditions between the different missions, we do not believe the change in VSL bromine from STRAT to ATTREX represents a long-term trend. More data are required in the TTL to better define the possible range of variation of the shorter-lived organic bromine species. Based on the densest sampling in the Western Pacific during ATTREX 2014, the measurements demonstrate the significant contribution of VSL_{org} of ~18% to the input of stratospheric bromine to the lower stratosphere.

We calculated that, during ATTREX, the average level of measured bromine resulted in 20% of total ozone destruction in the tropical lower stratosphere. However, potential changes in the ocean−air flux or a rise in seaweed cultivation could increase VSL_{org} emissions, leading to an even larger percentage of ozone depletion. Further observations with high-altitude aircraft will improve our understanding of the role of VSL_{org} in the composition of the tropopause region and the processes occurring in the TTL, diminish the uncertainties of the amount of Br_y that enters the stratosphere, and ascertain whether VSLBr is changing in this critical region.

Materials and Methods

GWAS is a modified version of the previous Whole Air Sampler described elsewhere (26, 27, 30, 31). The instrument consists of 90 custom-made, Silonite-coated (Entech Instruments), 1.3-L stainless steel canisters with Parker Series 99 solenoid valves (Parker-Hannifin), mounted onto a custom-made support. A welded, stainless steel manifold connects to two metal bellows compressor pumps (Senior Aerospace) to flow ambient air through a custom inlet at flow rates ranging from 2 to 8 standard liters per minute, depending on altitude. The manifold and canister module temperatures were controlled to remain within the range of 0–30 °C. GWAS is a fully automated instrument controlled from the ground through an Ethernet interface. The Data System Module (DSM), inside the aircraft, interacts remotely with a ground laptop via aircraft networks. Parameters to fill the canisters, flush the manifold, and control the temperature can be predetermined in the DSM to fill the canisters automatically in case of

communication failure. However, the parameters can be manually set from the ground to improve the sampling collection at different altitudes.

During the ATTREX campaign, the canisters were filled to ~3 standard atmospheres (40 psi) using about 25 s at 14 km and 90 s at 18 km. Samples were analyzed in the field using a high-performance gas chromatograph (Agilent Technology 7890A) and mass spectrometer with mass selective, flame ionization, and electron capture detector (Agilent Technology 5975C). Samples were concentrated on an adsorbent tube at −38 °C with a combination of cryogen-free automation and thermal desorber system (CIA Advantage plus UNITY 2; Markes International). The oven temperature profile was −20 °C for 3 min, then 10 °C/min to 200 °C, and 200 °C for 4 min, for a total analysis time of 29 min. Under these sampling conditions, the precision was compound/concentration-dependent, and ranged from <2% to 20%. Calibration procedures as well as mixing ratio calculations are described elsewhere (27).

The Community Atmospheric Model, version 4, coupled with comprehensive tropospheric and stratospheric chemistry, CAM-Chem, included in the Community Earth System Model (version 1.1.1) (32), was used to compare the observations of brominated compounds measured during ATTREX (e.g., Fig. S5 A and B). The chemical mechanism was based on Model for Ozone and Related chemical Tracers, version 4, and was extended to explicitly represent the chemistry of VSLBr. It included bromine photochemistry, dry−wet deposition, and heterogeneous chemistry on sea salt aerosols and ice particles. A detailed description of the chemistry scheme as well as the emission inventories can be found in previous studies (4, 20). Model simulations were run in specified dynamics mode using analysis from the NASA Goddard Global Modeling and Assimilation Office using the Goddard Earth Observing System Model, Version 5 (GEOS5). The horizontal resolution is 1.25° (longitude) × 0.9° (latitude) with 56 vertical levels (from the surfaces to ~10 hPa), and a temporal resolution of 30 min. CAM-Chem validation of the tropical vertical profile of speciated Br_y (e.g., BrO) has been reported in a previous study (4), where it shows an excellent agreement with balloon measurements performed at Teresina, Brazil.

Back-trajectories were calculated with the Met Office's NAME (33), a Lagrangian model successfully used in other studies (e.g., ref. 21). Slightly different from the CAM-Chem resolution, tracer particles were moved through the model atmosphere by a combination of 0.352° longitude and 0.235° latitude (horizontal resolution of ~25 km, 31 vertical levels below 19 km) mean wind fields calculated by the Met Office's Unified Model at 3-h intervals and a random walk turbulence scheme. NAME was run backward in time to determine where the air measured at a particular location may have originated. For each ATTREX flight, 15,000 particles were released from all flight track points where GWAS samples were taken (box dimensions of 0.1° × 0.1° × 0.3 km). The trajectories were followed backward for 12 d, and the fraction of particles that crossed the 5- and 1-km-altitude level was calculated to indicate air masses of low tropospheric and boundary layer origin, respectively. These were used to identify the sample-to-sample and flight-to-flight variations of air masses in the TTL (21).

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