Maximizing Degrees of Freedom in MAX-DOAS Retrievals of BrO from Remote Tropical Marine Mountaintops

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Abstract: We are developing sensitive atmospheric vertical profile retrieval capabilities from MAX-DOAS sensors on tropical island mountaintops. Particularly, we target BrO which has significant impacts on the lifetime of greenhouse gases such as O_3 and CH_4.

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1. Motivation

Tropospheric halogens, including bromine, are emitted from oceans into the atmosphere in organic form, and as sea spray aerosols. Heterogeneous chemistry on acidic aerosol surfaces lead to the release of bromide (and chloride) to the gas-phase, and leaves aerosols depleted in bromide (and chloride) relative to their sodium ratios in sea-water. Halogens catalytically destroy ozone (O_3), modify the concentrations and cycling of hydrogen oxide radicals (HO_x = OH + HO_2) and nitrogen oxide radicals (NO_x = NO + NO_2), oxidize atmospheric mercury, and contribute to nanoparticle formation and growth. The impacts on O_3, HO_x, and NO_x, in turn lead to net increases in the lifetime of climate warming gases, particularly methane.

Sea-spray is widely considered to be the largest source of tropospheric halogens globally. However, state-of-the-art atmospheric models differ in their treatment of this halogen source, and predict elevated BrO to be widespread over oceans, while field observations rarely confirm predictions of such elevated BrO. The tendency of atmospheric models to over-predict BrO over remote oceans is currently not understood, and remains poorly tested at tropical latitudes, where ~75% of the global O_3 and CH_4 destruction occurs. We hypothesize that a missing process is operative that converts gas-phase BrO_x (= Br + BrO) into gas-phase Br_y, possibly reactions of BrO_x with oxygenated volatile organic compounds (OVOC).

2. Introduction to Methods

Differential Optical Absorption Spectroscopy (DOAS) is a technique whereby broadband features are removed from signals in order to measure differential absorption features with less optical density [1]. Species that are amenable to DOAS measurement include oxygen collision induced absorption (O_2-O_2 = O_4), NO_2, O_3, the halogen radicals: BrO and IO, and OVOC species HCHO and CHOCHO.

The primary data product of a DOAS measurement is a differential Slant Column Density (dSCD), the integrated concentration of an absorber along the light path relative to a reference measurement. Characterizing the reference Slant Column Density (SCD_{Ref}) is necessary to obtain the more useful Slant Column Densities (SCD) for the various measurements.

In order to retrieve information on the vertical distribution of absorbers from DOAS data, the geometry of measurement must be varied. Zenith Sky DOAS (ZS-DOAS) collects scattered light in a zenith pointing geometry utilizing the motion of sun to obtain information along different light paths. Multi-AXis DOAS (MAX-DOAS) gains information along different light paths by changing telescope pointing. When ZS-DOAS and/or MAX-DOAS measurements are combined with radiative transfer modelling (RTM) they can be used to retrieve profiles of atmospheric gases, and assess the vertical column densities (VCD).

Profiles are retrieved using optimal estimation, an additional product of which is a square matrix of averaging kernels (AVK). The diagonal elements of AVK indicate the independent information provided by measurements about a particular point in a profile. Hence, the trace of AVK indicates the number of pieces of information provided by measurements independent of a priori assumptions, the degrees of freedom (DoF). Off diagonal terms of the AVK indicate the interdependence of points in the retrieved profile, and are roughly an inverse measure of resolution.

The information of profiles is maximized where the variation in light path geometry is greatest. For ZS-DOAS this is in the stratosphere at high solar zenith angle (SZA), typically retrieving 1-2 DoF in the stratosphere with low resolution. For MAX-DOAS the maximum information content is obtained near the instrument altitude, typically retrieving 1 DoF with high resolution at this altitude, and up to one additional DoF distributed over the remaining atmosphere. Both sampling methods struggle to obtain information content in the free troposphere. If MAX-DOAS sensors are placed on high mountain observatories, measurements in the free troposphere are unobstructed by aerosols, and the profiling capabilities are an area of active research. Mountaintop observatories on tropical oceanic islands provide unique long term access to the tropical free troposphere, removed from anthropogenic emissions.

In the tropics, the BrO partial VCDs in the troposphere and stratosphere are roughly equal [2]. This allows for meaningful information to be gained both above and below the free troposphere and maximizes the potential to further probe it. We aim to achieve five degrees of freedom (5 DoF) in daily BrO retrievals.

3. Data Description

Since February 2017 we have deployed MAX-DOAS instruments on two remote tropical marine mountaintops, Mauna Loa Observatory (MLO) at 19.5°N, 155.6°W, 3.4 km AMSL, and Maïdo Observatory (Maïdo) at 21.1°S, 55.4°E, 2.2 km AMSL. We measure strong absorbers: O_4 (at 360 and 477 nm), NO_2 (at 360 and 430 nm), and O_3 (at 330 and 485 nm); halogen radicals: BrO and IO; and OVOC: HCHO and CHOCHO.

A similar MAX-DOAS instrument was previously deployed at MLO in 2014, with most of the same capabilities listed above. Also in 2014, we operated an airborne MAX-DOAS (AMAX-DOAS) instrument as part of The CONvective TRansport of Active Species in the Tropics (CONTRAST) field campaign. This included two research flights in proximity to MLO, namely RF01 on January 11, 2014 which probed a stratospheric intrusion over Hawaii, and RF17 on February 28, 2014 which observed more ordinary tropospheric conditions.

4. Toward a Five Degrees of Freedom Retrieval of BrO

The mountaintop sites minimize complications such as aerosol present at the surface, and potentially also have access to useful information in downward viewing geometries, as such they are expected to have inherent advantages over instruments placed at sea-level. Furthermore, recent advances BrO retrievals have pushed beyond 2 DoF in both ZS-DOAS retrievals of the stratosphere and MAX-DOAS retrievals of the troposphere as described below. Bringing these improvements to bear and combining the stratospheric and tropospheric retrievals into a single optimal estimation we aim to achieve daily atmospheric profiles of BrO with 5 DoF to better understand atmospheric bromine in the tropics.

BrO is a photochemically active atmospheric radical, as a result its concentration changes with actinic flux. This is especially relevant around twilight when the actinic flux varies rapidly. This presents a challenge for ZS-DOAS retrievals which utilize the same variation in the sun's geometry to obtain information on the stratosphere. Accounting for this by coupling the chemical change into the retrieval allows existing measurements to be be more effectively leveraged and raises the information content of ZS-DOAS retrievals achieve up to 2.5 DoF, primarily in the stratosphere [3].

Airborne platforms provide a partial solution to the lack of free tropospheric information from ZS- and MAX-DOAS measurements. Physically moving the instrument through the atmosphere yields extensive profiling capability (up to 30 DoF can be obtained for an aircraft profile) but only at snapshots in time. The information from aircraft profiles can be utilized twofold by measurements from other platforms. First, the distribution of an absorber in the atmosphere impacts how it appears to different measurement geometries, it's air mass factor (AMF). The high resolution of aircraft profiles can allow for more accurate calculations of relevant tropospheric AMF. Second, aircraft profiles can provide a statistical set of a priori profiles for retrievals. Aircraft measured BrO profiles over the western and eastern Pacific Ocean provide such data for both purposes [4-7].

Colocated aircraft and ship-based MAX-DOAS retrievals in the tropics during TORERO [4], demonstrate improved AMFs obtained from aircraft profiles and SCDs rather than dSCDs are critical to accurate profile retrieval aloft. Utilizing aircraft profiles to obtain an accurate SCD_{Ref} and AMFs for use in the ship-based retrieval achieved better agreement between measurements aloft where the latter has less skill. The CONTRAST BrO profiles are

leveraged for mountaintop retrievals near in time from MLO in order to achieve preliminary SCD_{Ref} for retrievals. Further they are utilized as a basis for possible profile shapes aloft.

Ground based MAX-DOAS at Pensacola, Florida [8] corroborate the importance of SCD_{Ref}. In the absence of aircraft profile or other direct measurement of the profile aloft, SCD_{Ref} was obtained by iteratively assessing the consistency of SCD_{Ref} with retrieved profiles, until convergence was achieved. Actively retrieving SCD_{Ref} in this way adds 0.5 DoF to a dSCD retrieval for a total of up to 2.5 DoF in the troposphere. Given that advantages of the mountaintop location, and the availability of aircraft data for specific case studies we expect to replicate or even improve on this performance.

4. References

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