Final Author Comments to reviewers of amt-2019-195,

1. (1) Anonymous Referee #3 (pages 1-3)
2. (2) Anonymous Referee #4 (page 5-end)

<u>To anonymous Referee #3</u>

We thank the referee #3 for constructive comments on the manuscript amt-2019-195, "Comparison of Optimal Estimation HDO/H2O Retrievals from AIRS with ORACLES measurements." We have addressed all comments from the referee.

Below are (1) comments from the referee, (2) our author's response **in bold** and (3) author's changes in the manuscript.

<u>Specific comments</u>

Comment 1:

(1) l48-57: Another instrument that provided HDO measurements was Envisat MIPAS. For instance: Lossow, S., Steinwagner, J., Urban, J., Dupuy, E., Boone, C. D., Kellmann, S., Linden, A., Kiefer, M., Grabowski, U., Glatthor, N., Höpfner, M., Röckmann, T., Murtagh, D. P., Walker, K. A., Bernath, P. F., von Clarmann, T., and Stiller, G. P.: Comparison of HDO measurements from Envisat/MIPAS with observations by Odin/SMR and SCISAT/ACE-FTS, Atmos. Meas. Tech., 4, 1855–1874, https://doi.org/10.5194/amt-4-1855-2011, 2011.

(2) We agree and will add a citation to Envisat/MIPAS and other contemporary satellite instruments that measure stratospheric HDO. This will be placed in the text immediately before the paragraph on satellite retrievals of *tropospheric* HDO.

(3) Changes to text, new paragraph added (l48) and the new references have been added to the end of the manuscript.

"Early remote sensing of atmospheric HDO was made by the ATMOS (Atmospheric Trace Molecule Spectroscopy) mission on the Space Shuttle (Rinsland et al., 1991; Irion et al., 1996; Moyer et al., 1996; Kuang et al., 2003), retrieving in the upper troposphere/lower stratosphere. Global stratospheric HDO measurements have been provided by satellite instruments including Envisat/MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) (Steinwagner et al., 2007, 2010; Lossow et al., 2011), Odin/SMR (Sub-Millimetre Radiometer) (Murtagh et al., 2002; Urban et al., 2007), and SCISAT-1 (Scientific Satellite)/ACE-FTS (Atmospheric Chemistry Experiment fourier transform spectrometer) (Bernath et al., 2005; Nassar et al., 2007; Lossow et al., 2011; Randel et al., 2012). Atmospheric columns densities of HDO and H2O have been retrieved from Sentinel-5 Precursor/TROPOMI (Tropospheric Monitoring Instrument) (Schneider et al., 2020)."

Comment 2:

(1) l130-131: Are these mean winds and surface pressure during the aircraft campaign (September 2016) or do they refer to a specific date and time?

(2) These are mean winds and surface pressure from MERRA2. We will modify a sentence in the Figure 1 caption.

(3) Changes to text, modified Figure 1 caption:

"Superimposed on the map are the September 2016 monthly mean 700-hPa winds (white vectors) and surface pressure (white isobars), along with the approximate biomass burning region (green rectangle)."

Comment 3:

(1) l243-256: If it is not too much extra work, I would suggest to combine Figs. 2 and 3 in a single figure, e.g., by using different colors for the different matching criteria.

(2) We will combine Figures 2&3 with loose-constraint AIRS FOV (open squares) and close-constraint AIRS FOV (solid black squares).

Comment 4:

(1) l291-292: Adjust y axis range to -200 ... +6200 m (or similar)?

(2) We have changed the y axis range accordingly.

(3) Revised Figure 4 (formerly Figure 5).

Comment 5:

(1) l299-300: The caption says "RMS (standard deviation)", but RMSˆ2 = BIASˆ2 + STDDEVˆ2, I think? Are these numbers standard deviations or RMS errors?

(2) These numbers are standard deviations. The convention in our community has been to not include bias in the RMS. We will clarify in the text that bias is not included in our RMS calculations.

(3) New sentence added to Table 2 caption: "The reported RMS here is the standard deviation, not including the bias."

Comment 6:

(1) l315: It may help the reader to say that G_R refers to the gain matrix of the HDO/H2O retrieval.

(2) We have modified the text accordingly.

(3) Text modified to, **"**where $\boldsymbol{G_R} = (\boldsymbol{G_z^D} - \boldsymbol{G_z^H})$ is the gain matrix of the HDO/H_2O retrieval".

Comment 7:

(1) l316: Which systematic errors and interference errors have been considered here?

(2) We have considered random error due to noise, and radiative interference errors due to CH_4, N_2O, surface emissivity, effects of temperature, and clouds.

(3) New sentence added: "Interference errors are due to CH_4, N_2O, surface emissivity, effects of temperature, and clouds."

Comment 8:

(1) l316-318: Looking at the averaging kernels, there are likely quite significant correlations being found in retrieval covariance S?

(2) Yes, the reviewer is correct. All of our retrieval products have significant covariation between levels and species but these are taken into account for process studies by appropriate use of the supplied uncertainties and in assimilation studies through use

of the averaging kernel and observation error covariances in the assimilation cost function.

(3) No change to the text.

Comment 9:

(1) l333-334: [Figure caption] Maybe say again that the estimated error is obtained from optimal estimation
retrieval theory and the empirical error is obtained from the satellite-aircraft comparison, to help the reader?

(2) **We have modified the text accordingly.**

(3) New sentence added to figure caption: "The empirical error is obtained from the statistics of the satellite-aircraft comparison, while the estimated error is obtained from optimal estimation retrieval theory."

Comment 10:

(1) l344-348: Based on these error estimates, can the AIRS HDO/H2O ratio retrievals be considered useful for further scientific analysis?

(2) **Yes, the AIRS HDO/H2O ratio retrievals are useful for scientific analysis. We will clearly state this in the Conclusions.**

(3) New sentence added to end of Conclusions, "The errors are sufficiently small that the AIRS HDO/H_2O ratio retrievals are useful for scientific analysis. This long term global data record has much potential utility."

Comment 11:

(1) l357-359: Not sure the team list is actually needed?

(2) The AMT publication guide specifies to use this format.

(3) No change to the text.

Technical corrections - **We have made all technical corrections as listed below:**
l24 and l44: ... HDO/H2O _ratio_
l81: D/H -> HDO/H2O
l85, l138, l226, l270 and other places: use lower case section headings
l151: _the_ forward model
l169: DeSouza-Machado
l176: of _the_ satellite retrievals
l213: completed _by_ applying
l258-259: Labels (a) and (b) are missing: **We have added labels (a) and (b) to Figure 3 (formerly Figure 4).**
l332: shows _that_ the empirical error
l340-341: acronym for WISPER does not need to be repeated: **acronym deleted.**
l467: paper title is formatted as a hyperlink: **hyperlink removed.**

We have also discovered the following typographical errors and corrected them:

p. 3, line 55 and p. 5 line 96: change Level 1b to Level 1**B**

p. 4, line 71: Change Fu et al., 2013 to **R.** Fu et al., 2013.
p. 5, line 96: Change Level 1b (L1b) to ‘Level 1B (L1B)’
p. 8 line 141: Change Fu et al. 2013 to **D.** Fu et al., 2013).

<u>To anonymous Referee #4</u>

We thank the referee #4 for constructive comments on the manuscript amt-2019-195, "Comparison of Optimal Estimation HDO/H2O Retrievals from AIRS with ORACLES measurements." We have addressed all comments from the referee.

Below are (1) comments from the referee, (2) our author's response **in bold** and (3) author's changes in the manuscript.

<u>Specific comments</u>

Comment 1:

(1) Lines 92-93: Is AMSU used in the retrieval in any way? Not sure you really need to include its introduction here as you are not using the golf ball configuration (9xAIRs + 1xAMSU IFOV).

(2) The reviewer is correct that the AIRS HDO retrieval does not use AMSU.

(3) Section 2.1 text has been modified to remove the 2-sentence introduction to AMSU. Instead, one sentence defines the horizontal resolution: "These footprint observations have a horizontal resolution of approximately 13.5 km at nadir."

Comment 2:

(1) Line 116: The reference for WISPER, if still in preparation are there any additional technical reports etc that could also be added?

(2) The reference for WISPER is still in preparation. AMT allows the gray literature (e.g. conference proceedings) if nothing else is available so we additionally cite an AGU abstract, Henze et al. 2017.

(3) New citation added: Henze and Noone, 2017,
Henze, D., and Noone, D.: *The Dependence of Entrainment and Drizzle in Marine Stratiform Clouds on Biomass Burning Aerosols Derived from Stable Isotope and Thermodynamic Profiles,* AGU Fall Meeting, New Orleans, Louisiana, United States, Abstract A11C-0048, 2017.

Comment 3:

(1) Table 1: Why are there some large discrepancies between the number of collocations and others have lower or no reduction in matchups when the tighter lat/lon constraint is applied? Maybe some additional information for context in the table header would be useful for readers unfamiliar with the ORACLES campaign.

(2) The reviewer has a good point. It should be better explained here that the loose constraint is a large rectangle aligned with parallels of latitude and meridians of longitude. All flights except two (Sep 2, 2016, and Sep 14, 2016) had large rectangles because the aircraft flew along the diagonal of the rectangle (see Figure 2). Sep. 2 and Sep. 14, 2016, had different flight patterns so we used smaller latitude/longitude shapes to constraint AIRS data on those days. The tighter constraint is matched AIRS geolocations and aircraft FOVs within 0.3 degrees of each other.

(3) New text has been added to the body of Sec. 4.1:

We have replaced the text "Within each flight are several profiles each spanning 1 to 3 degrees (or ~ 100 to 300 km), so measurement pairs are typically within 3 degrees (Fig. 2)."
With the revised text:
"The loose constraint (Table 1 column 1, Fig. 2 open circles and Fig. 4a) is that, for an aircraft vertical profile (~ 100 to 300 km in length), all AIRS geolocations within the same rectangle of maximum to minimum latitude and maximum to minimum longitude are selected. The only exceptions were the aircraft flights of 9/2/2016 and 9/14/2016, which had different flight patterns and smaller shapes were used to constrain AIRS geolocations. The tighter constraint (Table 1 column 2, Fig. 2 closed circles and Fig. 4b) is to match only AIRS geolocations within 0.3 degrees (30 km) of the aircraft flight track."

Comment 4:

(1) Line 222-223: Do you get 1 DOF between 750-350 hPa?
(2) Yes, most retrievals have approximately 1 DOF between 750-350 hPa. Most of the sensitivity of AIRS to HDO is at pressure levels of 750 hPa to 350 hPa so most of the information is coming from these levels.
(3) No change to text.

Comment 5:

(1) Line 239: Is the DOF threshold for a sub-column between 750-350 hPa?
(2) No, the DOF threshold is for the total column of AIRS HDO/H_2O. This DOF threshold is used merely as a way to filter for the retrievals with the highest information content.
(3) New Text added to Section 4.1:
"Following Worden et al. (2007) and Brown et al. (2008), we filter data for a reasonable threshold of standard nadir data product DegreesOfFreedomForSignal (DOFS) > 1.1, but include all values of AverageCloudEffOpticalDepth. Data product DOFS is the trace of the averaging kernel, and is a measure of the number of independent parameters for the retrieved HDO/H_2O profile. AverageCloudEffOpticalDepth is the retrieved cloud mean optical depth at wavenumbers from 975 to 1200 cm^{-1} from the final retrieval step (e.g., the same for all species) (Kulawik et al., 2006)."

Comment 6:

(1) Line 240: Where does the cloud optical depth information come from? Is it a retrieval output? Is there any uncertainty information associated with the cloud information, if so is it propagated?
(2) The cloud optical depth is standard retrieval output, retrieved for a non-scattering cloud reported from the values at the final sequential retrieval step. The uncertainty information associated with the cloud is propagated. The AIRS cloud optical depth is retrieved the same way as the TES cloud optical depth, new citation: Kulawik, S. S., Worden, J., Eldering, A., Bowman, K., Gunson, M., Osterman, G. B., Zhang, L., Clough, S., Shephard, M. W. and Beer, R.: Implementation of cloud retrievals for Tropospheric Emission Spectrometer (TES) atmospheric retrievals: part 1. Description and characterization of errors on trace gas retrievals, J. Geophys. Res., 111, D24204, doi:10.1029/2005JD006733, 2006.

(3) New text, New sentence added: “Interference errors are due to CH_4, N_2O, surface emissivity, effects of temperature, and clouds.”
And also new text in Section 4.1,
“Following Worden et al. (2007) and Brown et al. (2008), we filter data for a reasonable threshold of standard nadir data product DegreesOfFreedomForSignal (DOFS) > 1.1, but include all values of AverageCloudEffOpticalDepth. Data product DOFS is the trace of the averaging kernel, and is a measure of the number of independent parameters for the retrieved HDO/H_2O profile. AverageCloudEffOpticalDepth is the retrieved cloud mean optical depth at wavenumbers from 975 to 1200 cm^{-1} from the final retrieval step (e.g., the same for all species) (Kulawik et al., 2006).”

Comment 7:
(1) Figures23: A little colour/shading would be useful to help distinguish land/ocean.
It is difficult to see the aircraft track through the AIRS IFOV markers. How many aircraft profiles are each subfigure?
(2) We will modify the Figures 2 and 3 to be easier to read. There are typically 3 to 6 aircraft profiles per subfigure. They overlap spatially as the aircraft flies the same diagonal path.

Comment 8:
(1) Figure 4: Subfigure headings are missing (a,b).
(2) We have added the subfigure headings (a) and (b) to the figure.
(3) Revised Figure, now renumbered as Figure 3.

Comment 9:
(1) Line 288: Little or no difference to a priori between 800 hPa-surface, is AIRS really adding anything here in the PBL? Is the averaging kernel not setting the difference between $(x - xa)$ residual to/or close to zero?
(2) The reviewer has an excellent point. In most cases AIRS does not have much sensitivity to the PBL deuterium content. Any differences between the PBL *a priori* will therefore reflect the diagonal of the averaging kernel, plus the cross terms that describe the sensitivity of the PBL estimate to the true state in the rest of the atmosphere.
(3) Since in most cases AIRS does not have much sensitivity to PBL HDO, we have modified the line 343-344 in the manuscript,
"We have shown that AIRS-only retrievals have sensitivity to HDO from the middle troposphere to the boundary layer."
to:
"We have shown that AIRS-only retrievals have sensitivity to HDO in the middle and lower troposphere."

Comment 10:
(1) Section 5: Is this a description of the a posteriori error? When you say you are characterising the error budget I would expect some account of the collocation/

representativeness uncertainty due to the mismatch with the aircraft. I think you might just need to change the wording on line 305 to make this clearer.

(2) Our response to the reviewer is, yes, we are referring to the *a posteriori* error. We will make the wording on lines 305 and 325-327 clearer as detailed below.

(3) At the start of Section 5. Error Estimation, we will modify:

"... we characterize the error budget for AIRS and assess this error by comparison with the ORACLES aircraft measurements."

To:

"... we characterize the *a posteriori* error budget for AIRS HDO/H_2O and assess this error by comparison with the ORACLES aircraft measurements."

At lines 325-327, discussing differences between the estimated error from OE and empirical error from the comparison, we will modify

"These differences are likely due to atmospheric variability as we do not have exact matchups between the AIRS data and aircraft measurements."

To:

"These differences between the OE estimated error and the empirical error are likely due to uncertainties in atmospheric variability in space and time and in the collocation between satellite retrieval and aircraft measurements. The instrument operator (Eq. 1) accounts for error due to the mismatch in *vertical* sensitivity between the satellite retrieval and aircraft *in situ* vertical profiling. In the cases where AIRS is compared to *in situ* measurements without the instrument operator, there is an additional smoothing error (Table 2). The instrument operator does not account for error due to *horizontal* mismatch. The close coincidences are all within 30 km (0.3 degrees), but given time differences, and the AIRS 15-km nadir footprint and limited *in situ* measurement, the satellite and aircraft are not necessarily measuring the same airmass. There is a collocation error on the order of ~10 per mil due to horizontal collocation/representativeness uncertainty."

<u>Technical Comments</u>

(1) Line 206: in situ – should be in italics

(2) We have made *in situ* italicized every time it appears in the manuscript.

Title Page

Comparison of Optimal Estimation HDO/H_2O Retrievals from AIRS with ORACLES measurements

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Abstract

In this paper we evaluate new retrievals of the deuterium content of water vapor from the Aqua Atmospheric InfraRed Sounder (AIRS) with aircraft measurements of HDO and H_2O from the ObseRvations of Aerosols above Clouds and their intEractionS (ORACLES) field mission. Single footprint AIRS radiances are processed with an optimal estimation algorithm that provides vertical profiles of the HDO/H_2O ratio, characterized uncertainties, and instrument operators (i.e., averaging kernel matrix). These retrievals are compared to vertical profiles of the HDO/H_2O ratio from the Oregon State University Water Isotope Spectrometer for Precipitation and Entrainment Research (WISPER) on the ORACLES NASA P-3B Orion aircraft. Measurements were taken over the Southeast Atlantic Ocean from 31 August to 25 September 2016. HDO/H_2O is commonly reported in δD notation, which is the fractional deviation of the HDO/H_2O ratio from the standard reference ratio. For collocated measurements, the satellite instrument operator (averaging kernels and a priori constraint) is applied to the aircraft profile measurements. We find that AIRS δD bias relative to the aircraft is well within the estimated measurement uncertainty. In the lower troposphere, 1000 to 800 hPa, AIRS δD bias is -6.6‰ and the Root Mean Square (RMS) deviation is 20.9‰, consistent with the calculated uncertainty of 19.1‰. In the mid-troposphere, 800 to 500 hPa, AIRS δD bias is -6.8‰ and RMS 44.9‰, comparable to the calculated uncertainty of 25.8‰.

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1. Introduction

The deuterium content of tropospheric water vapor is sensitive to the different types of atmospheric moisture sources such as evaporation from the ocean or land and the processing that occurs during transport such as mixing or condensation (e.g., Craig, 1961; Dansgaard, 1964; Galewsky et al., 2016). Condensation and precipitation preferentially remove the heavier HDO isotopologue from the gas phase relative to the parent isotopologue H_2O, whereas evaporation of precipitation at lower altitudes in the atmosphere can enrich HDO relative to H_2O vapor. These unique, isotopic properties allow the HDO/H_2O ratio to be a tracer for the origin, condensation and evaporation history of an air parcel, thus useful for evaluating changes to the water cycle (e.g., Worden et al., 2007; Noone, 2012; Galewsky et al., 2016).

Early remote sensing of atmospheric HDO was made by the ATMOS (Atmospheric Trace Molecule Spectroscopy) mission on the Space Shuttle (Rinsland et al., 1991; Irion et al., 1996; Moyer et al., 1996; Kuang et al., 2003), retrieving in the upper troposphere/lower stratosphere. Global stratospheric HDO measurements have been provided by satellite instruments including Envisat/MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) (Steinwagner et al., 2007, 2010; Lossow et al., 2011), Odin/SMR (Sub-Millimetre Radiometer) (Murtagh et al., 2002; Urban et al., 2007), and SCISAT-1 (Scientific Satellite)/ACE-FTS (Atmospheric Chemistry Experiment fourier transform spectrometer) (Bernath et al., 2005; Nassar et al., 2007; Lossow et al., 2011; Randel et al., 2012). Atmospheric columns densities of HDO and H_2O have been retrieved from Sentinel-5 Precursor/TROPOMI (Tropospheric Monitoring Instrument)

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(Schneider et al., 2020).

In the last decade, satellite retrievals of tropospheric water vapor isotopic composition (HDO and H_2O) have been developed, including Envisat/SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) (Frankenberg et al., 2009), IASI (Infrared Atmospheric Sounding Interferometer) aboard the MetOp satellites (Herbin et al., 2009; Schneider and Hase, 2011; Lacour et al., 2012), and TES (the Tropospheric Emission Spectrometer) on the Aura spacecraft (Worden et al., 2006; Worden et al., 2007). More recently, Worden et al. have developed HDO retrievals from the Aqua Atmospheric InfraRed Sounder (AIRS) single footprint Level 1B radiance data (Worden et al., 2019). These AIRS retrievals are the subject of the present comparison with aircraft data.

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Satellite HDO measurements have been utilized to study tropical carbon/water feedbacks (Wright et al., 2017), moist processes in deep convection (e.g. Worden et al., 2007), and the global partitioning of transpiration to evapotranspiration (Good et al., 2015). A decadal record of HDO has promise in characterizing global shifts in moisture sources and atmospheric water balance in response to warming, climactic variability, and land-use. For example, Bailey et al. (2017) shows that a record of free-tropospheric HDO/H_2O would provide an observational constraint on changes in the tropical water balance (evaporation minus precipitation) in response to shifts in ocean temperature. Wright et al. (2017) also shows that free-tropospheric deuterium measurements provide a fundamental new constraint in carbon / water dynamics in the Amazon. They use the TES isotope measurements to show that dry-season evapotranspiration is critical towards initiating the southern Amazon rainfall, which in turn is critical towards sustaining the Amazon rainforest (R. Fu et al., 2013). For these reasons a record of the deuterium content of water vapor from the long (17 years and continuing) record from AIRS holds significant potential to evaluate changes in the global water cycle.

This paper presents detailed comparisons between new AIRS measurements of the deuterium content of water vapor (or HDO/H_2O ratio) and accurate *in situ* HDO/H_2O measurements from an aircraft sensor during the NASA ObseRvations of Aerosols above Clouds and their intEractionS (ORACLES) field mission. In this paper, we denote the volume mixing ratios q_D for HDO, and q_H for H_2O. By standard convention, we report the isotopic abundance as δD (per mil or ‰) = $[(q_D/q_H)_{obs}/(q_D/q_H)_{std} - 1] * 1000$, where $(q_D/q_H)_{std}$= 3.11x10^{-4} based on the HDO/H_2O standard ratio for Vienna Standard Mean Ocean Water (SMOW).

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2. Instrumentation

2.1 AIRS instrument description

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The Atmospheric InfraRed Sounder (AIRS) on the NASA Aqua satellite is a nadir-viewing, scanning thermal infrared grating spectrometer that covers the 3.7 to 15.4 μm spectral range with 2378 spectral channels (Pagano et al., 2003, and Aumann et al., 2003). Launched on May 4, 2002, Aqua is in a sun-synchronous orbit at 705 km with an approximately 1:30 pm equator crossing-time as part of the A-Train satellite constellation. AIRS continues to make daily measurements of most of the globe with its wide cross-scanning swath of coverage. For HDO retrievals, the single footprint AIRS Level 1B (L1B) radiances are utilized. These footprint observations have a horizontal resolution of approximately 13.5 km at nadir. Absolute radiometric accuracy between 220 K and 320 K at all observation angles is better than 0.2 K (Pagano et al., 2003, 2008). The algorithm applied to AIRS radiances to yield HDO is described below in Sect. 3.1.

Deleted: The AIRS instrument makes collocated measurements with the Advanced Microwave Sounding Unit (AMSU) on the Aqua satellite. There are nine AIRS single footprint observations (nadir horizontal resolution of ~13.5 km) arranged in a 3 by 3 grid within a single AMSU footprint of ~45 km (Aumann et al., 2003).

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2.2 WISPER system for aircraft measurements

Aircraft measurements were made on the NASA P-3B Orion aircraft during the NASA ORACLES field mission. ORACLES is a five-year Earth Venture Suborbital (EVS-2) investigation with three Intensive Observation Periods (IOP) designed to study key processes that determine the climate impacts of African biomass burning aerosols in 2016, 2017, and 2018. The ORACLES experiment provided multi-year airborne observations from the NASA P-3B Orion and ER-2 aircraft over the complete vertical column of the key parameters that drive aerosol-cloud interactions in the southeast Atlantic Ocean region. The focus of the ORACLES field measurements was a biomass burning plume that advected west from the African continent to the Atlantic Ocean at 2 to 5 km altitude above sea level, ASL. Here we use data from the ORACLES 2016 IOP (ORACLES Science Team, 2017), and report on aircraft versus satellite comparisons from eight flights (Fig. 1 and Table 1).

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Water vapor isotopic abundances (HDO/H_2O and $H_2{}^{18}O/H_2{}^{16}O$) were measured *in situ* on the aircraft with the Oregon State Water WISPER system (Water Isotope Spectrometer

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for Precipitation and Entrainment Research, Henze et al., in prep.; Henze and Noone, 2017), which uses a modified commercial Picarro L2120-i δD/ δ^{18}O Ultra High-Precision Isotopic Water Analyzer. The measurement technique is cavity ring-down (CRD) spectroscopy (O'Keefe and Deacon, 1988; Berden et al., 2000; Gupta et al., 2009). The majority of measurements analyzed in this paper are located within the biomass burning plume, characterized by elevated H_2O (approximately 6000 ppmv) and elevated δD (-100 to -70‰). At these abundances of HDO/H_2O, the 1-Hz precision (1σ) of the measurements of δD is ±3‰, and the accuracy is ±6.5‰.

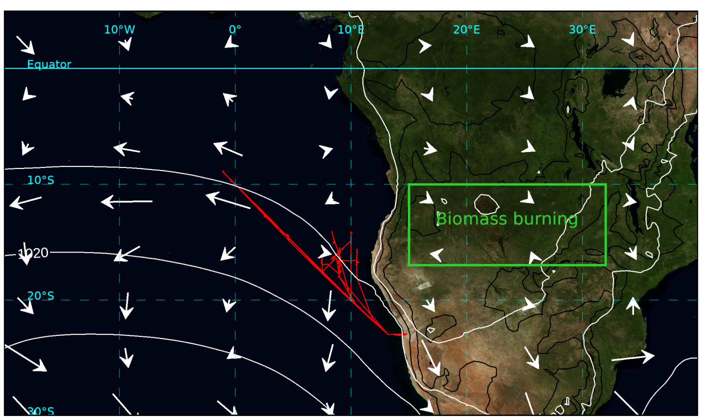

Figure 1. Selected flight tracks (red lines) of the NASA P-3B Orion aircraft during the ORACLES 2016 IOP used in this study, with corresponding flight dates listed in Table 1. Superimposed on the map are the September 2016 monthly mean 700-hPa winds (white vectors) and surface pressure (white isobars), along with the approximate biomass burning region (green rectangle).

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Deleted: Also shown is the biomass burning region (green rectangle), 700 hPa winds (white vectors), and surface pressure (white isobars).

Table 1. Summary of matches of AIRS and WISPER δD measurements during NASA ORACLES*.

Flight Date	Daily Number of Matched Profiles, loose lat/lon constraint.	Daily Number of Matched Profiles, tighter lat/lon constraint.
31-Aug-2016	138	26
2 Sep 2016	15	15
4 Sep 2016	102	26
10 Sep 2016	48	7
12 Sep 2016	18	4
14 Sep 2016	12	5
20 Sep 2016	11	4
25 Sep 2016	102	23
Total	**446**	**110**

*NASA ORACLES is the "ObseRvations of Aerosols above Clouds and their intEractionS" Earth Venture Suborbital Mission.

3 Satellite Retrieval

3.1 Retrieval algorithm

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The single footprint AIRS HDO profile data used in this work were produced using the retrieval algorithm, named the MUlti-SpEctra, MUlti-SpEcies, MUlti-Sensors (MUSES) algorithm (D. Fu et al., 2013, 2016, 2018, 2019; Worden et al., 2019). The MUSES algorithm can use radiances from multiple instruments including AIRS and other instruments (CrIS, TES, OMI, OMPS, TROPOMI, and MLS) to quantify geophysical observables that affect the corresponding radiance. The AIRS single footprint HDO profile retrievals have been described by Worden et al. (2019), and have heritage from the TES algorithm (Worden et al., 2004, 2006, 2007, 2011, 2012, 2013; Bowman et al. 2006, 2002). The Optimal Spectral Sampling (OSS) fast radiative transfer model (Moncet et al., 2008, 2015) for single footprint AIRS measurements has been integrated into the MUSES algorithm, in support of the operational data production towards the multi-decadal record of global HDO profiles. The supplement attached to this paper discusses the sensitivity of the retrievals to the choice of the forward model. The retrieval uses the optimal estimation (OE) method to quantify atmospheric HDO and H_2O (Worden et al. 2006, 2012, 2019). For both AIRS and TES retrievals, height discrimination of the HDO/H_2O ratio in the troposphere is provided by spectral resolution of pressure and temperature broadened absorption features of their corresponding lines (Beer et al., 2002). The algorithms and spectral microwindows are described by Worden et al. (2019). Chemical species CH_4, CO, HDO, and H_2O are jointly retrieved along with atmospheric temperature, surface temperature, land emissivity and clouds (Worden et al. 2012). The retrieval optimizes the ratio of HDO to H_2O, as opposed to either HDO or H_2O alone (Worden et al., 2019, 2012, 2006). AIRS radiances at wavelengths from 8 to 12 μm are used here, excluding the 9.6 μm ozone band. The parent molecule H_2O is retrieved at both 8 and 12 μm, but HDO is retrieved primarily from strong absorption lines in the 8 μm region (particularly in the wavenumber range 1210 to 1270 cm^{-1}). Cloud optical depth and cloud top pressure are jointly retrieved with the chemical species, using the approach described in Kulawik et al. (2006). The cloud-clearing approach (Susskind et al., 2003), utilized in AIRS operational products up to and including AIRS v6, where retrievals are reported on the 45 km Advanced Microwave Sounding Unit (AMSU) footprint, is not utilized here. As described by Worden et al. (2019), retrievals are performed on single AIRS 13.5-km footprints in order to preserve the Level 1B radiance noise characteristics (Irion et al., 2018; DeSouza-Machado et al., 2018).

For H_2O, the a priori constraint vectors come from NASA's Goddard Earth Observing System (GEOS) data assimilation system GEOS version 5.12.4 processing stream (Rienecker et al., 2008). These are produced by the Global Modeling and Assimilation Office (GMAO) at the NASA Goddard Space Flight Center (GSFC). The GMAO GEOS-5.12.4 water mixing ratios are linearly interpolated to the latitudes, longitudes, and log(pressure) levels of the satellite retrievals to generate the a priori profiles.

For all HDO retrievals, the initial profile of the $HDO/H_2{}^{16}O$ isotopic ratio is set equal to a simulated tropical profile (Worden et al., 2006). In the AIRS HDO product files, a priori HDO is defined as the product of the local a priori H_2O profile (GMAO GEOS-5.12.4) and one tropical a priori profile of the HDO/H_2O isotopic ratio (Worden et al., 2006). The initial guess profiles for H_2O are set equal to the a priori.

3.2 Method of comparison

The AIRS HDO/H_2O retrievals are matched up in space and time with the aircraft *in situ*

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HDO/H_2O measurements. A critical aspect of validating satellite retrievals is obtaining data that span the altitudes where the satellite has sensitivity to HDO/H_2O. AIRS data are sensitive to the HDO/H_2O ratio in the atmosphere from the surface up to approximately 10,000 m altitude. The aircraft samples HDO and H_2O from the surface up to 6000 m altitude, spanning most of the altitudes where the AIRS data are sensitive and therefore allowing us to validate AIRS HDO/H_2O with *in situ* measurements.

For direct comparison of AIRS HDO/H_2O with *in situ* HDO/H_2O, the AIRS instrument operator (averaging kernel and *a priori* constraint) is applied to the *in situ* data (see Eq. 1 below), as described by Rodgers (2000). This has the effect of smoothing the *in situ* data to the same resolution as the satellite retrievals. The averaging kernel matrix A is the sensitivity of the AIRS estimate to the true concentration in the atmosphere (Rodgers, 2000). The *in situ* profile with applied averaging kernel $x_{insituw/AK}$ is calculated jointly for HDO and H_2O using the AIRS operator:

$$x_{insituw/AK} = x_a + A_{xx}(x - x_a) \qquad (1)$$

Joint HDO/H_2O retrievals are performed on the logarithm of the volume mixing ratios, $x_D = \ln(q_D)$ and $x_H = \ln(q_H)$ (Worden et al., 2012, 2006). The data structure for AIRS HDO files is similar to TES HDO, with details provided by Herman et al. (2014).

For comparison with AIRS, the *in situ* HDO and H_2O profiles are extended to cover the full range of AIRS levels. In the boundary layer, from the surface up to the lowest altitude aircraft data, we assume constant values of HDO and H_2O set equal to the first aircraft measurement. In the range of aircraft data (up to 6000-m flight ceiling), the aircraft *in situ* HDO and H_2O data are interpolated to the levels of the AIRS forward model, smoothing fine scale features. In the layers above the aircraft maximum altitude, the profile is extrapolated using a scaled a priori profile. In this paper, all comparisons have been completed by applying Eq. 1.

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4 Validation

Validating the accuracy of AIRS HDO and H_2O retrievals is important for studies of the hydrologic cycle, exchange processes in the troposphere, and climate change. Comparisons of AIRS and TES over five years (2006-2010) indicate that the retrieval characteristics of the AIRS HDO/H_2O measurements have similar vertical resolution and uncertainty in the middle troposphere but with slightly less sensitivity in the lower troposphere (Worden et al., 2019). Worden et al. (2019) reported that the calculated uncertainty of AIRS HDO/H_2O is ~30 per mil for a tropospheric average between 750 and 350 hPa, with mean bias between TES and AIRS (TES-AIRS) for the HDO/H_2O ratio of ~-2.6 per mil and a latitudinal variation of ~7.6 per mil.

4.1 Comparison of AIRS with aircraft measurements

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ORACLES 8/31 to 9/25/2016 data comparison.

In this section, we describe comparisons between AIRS and ORACLES aircraft HDO measurements. First, time segments of each aircraft flight are identified where the aircraft profiled from the boundary layer up to approximately 6000 m altitude. To minimize the impact of atmospheric spatial and temporal variability, same-day AIRS measurements are selected for the same latitude/longitude rectangle as each aircraft profile (Fig. 2). These matched pairs are compared by the method described in Sect. 3.2. The loose constraint (Table 1 column 1, Fig. 2 and Fig. 4a) is that, for an aircraft vertical profile (~ 100 to 300 km in length), all AIRS geolocations within the same rectangle of maximum to minimum latitude and maximum to minimum longitude are selected. The only exceptions were the aircraft flights of 9/2/2016 and 9/14/2016, which had different flight patterns and smaller shapes were used to constrain AIRS geolocations. The tighter constraint (Table 1 column 2, Fig. 2 closed circles and Fig. 4b) is to match only AIRS geolocations within 0.3 degrees (30 km) of the aircraft flight track. The standard data retrieval quality flags for the retrieval are used in this analysis, which are based on the Aura TES data retrieval quality flags (Herman and Kulawik, 2018). For closer spatial coincidence, we also selected AIRS-aircraft measurement pairs within 0.3 degrees (Fig. 2). Following Worden et al. (2007) and Brown et al. (2008), we filter data for a reasonable threshold of standard nadir data product DegreesOfFreedomForSignal (DOFS) > 1.1, but include all values of AverageCloudEffOpticalDepth. Data product DOFS is the trace of the averaging kernel, and is a measure of the number of independent parameters for the retrieved HDO/H_2O profile. AverageCloudEffOpticalDepth is the retrieved cloud mean optical depth at wavenumbers from 975 to 1200 cm^{-1} from the final retrieval step (e.g., the same for all species) (Kulawik et al., 2006). Fig. 3(a) shows a representative 31 Aug 2016 comparison between aircraft water vapor δD from WISPER and the coincident AIRS retrieval. Fig. 3(b) shows the corresponding averaging kernels.

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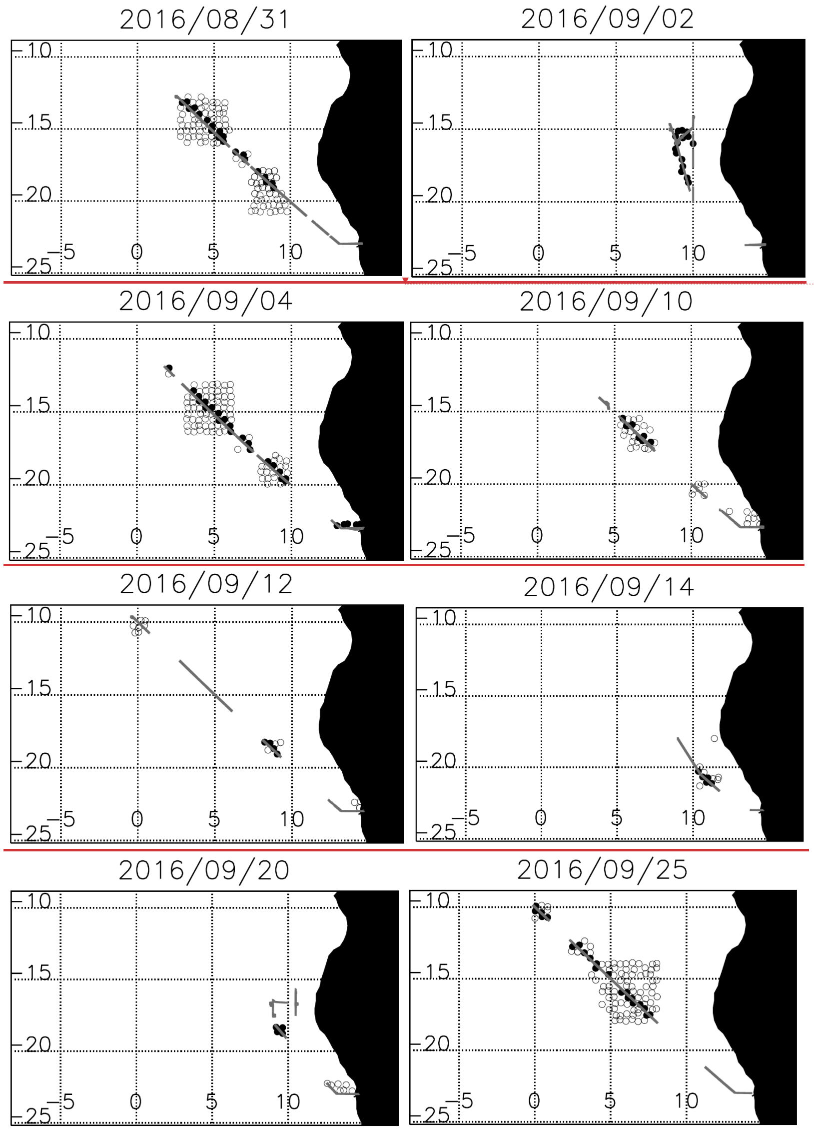

Figure 2. ORACLES aircraft profiles (thin grey line segments) over the southeast Atlantic Ocean to the west of Africa are matched to AIRS fields of view (FOVs) in loose spatial match (open circles) and tight spatial match within 30 km (closed circles) for eight

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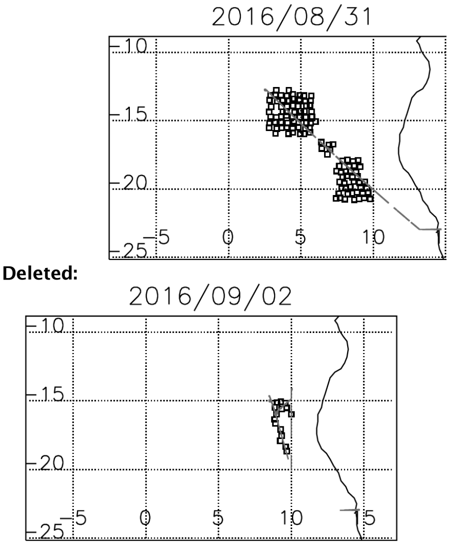

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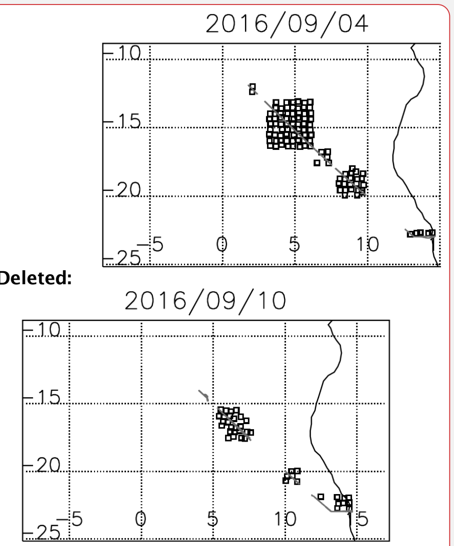

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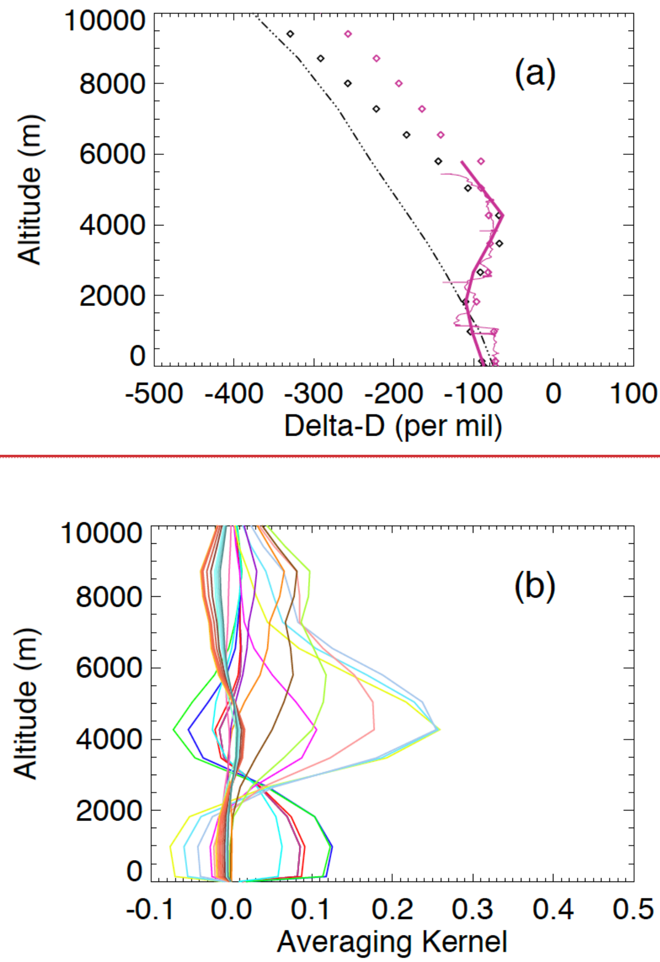
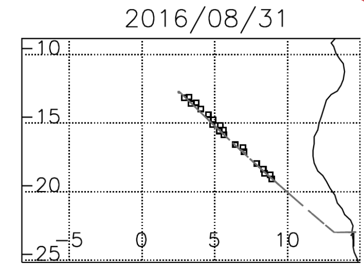


Figure 3. (a) Sample comparison of the δD profiles by aircraft and satellite over the southeast Atlantic Ocean during ORACLES on 31 August 2016: shown are AIRS δD (black diamond symbols), the prior δD (black dash-dot-dot line), nearest WISPER δD



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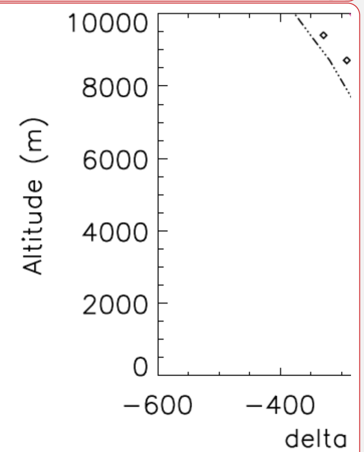

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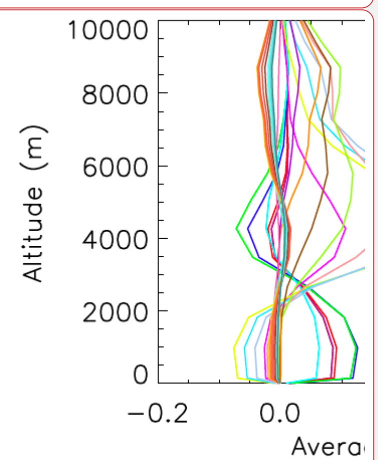

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(thin red line), WISPER δD interpolated to satellite levels (red diamonds), and the WISPER δD with the AIRS averaging kernel applied (thick red line).

(b) Averaging Kernel corresponding to same AIRS profile on 31 August 2016, color-coded by pressure level. Averaging kernels with the largest positive sensitivity below 2000 m are from the lowest altitudes.

4.2 AIRS bias correction

TES HDO/H_2O ratios are biased compared to model and *in situ* measurements (Worden et al., 2006, 2007, 2011). We assess whether AIRS HDO has a bias relative to *in situ* measurements. As described above, AIRS and TES show a small bias for the HDO/H_2O ratio of ~-2.3 per mil (Worden et al., 2019) after a bias correction is applied, so it is reasonable to see how well *in situ* and AIRS data agree if the TES bias correction is applied to the AIRS HDO. Herman et al. (2014) estimated the TES bias δ_{bias} by minimizing the difference between bias-corrected TES and *in situ* δD with TES operator applied:

$$\delta_{bias} = 0.00019 \times Pressure - 0.067 \quad (2)$$

We apply the TES δ_{bias} to the AIRS data to evaluate against ORACLES aircraft data. There are 446 matched profiles of AIRS and ORACLES within the same latitude/longitude boxes and 110 closely-matched profiles within 0.3 degrees or approximately 30 km (Fig. 2). Comparisons with averaging kernel applied are shown in Fig. 4 and Table 2. Over the range of aircraft data, 0 km to 6 km altitude, AIRS δD has a mean bias of -6.7‰ relative to the aircraft profiles, well within the estimated measurement uncertainty of both AIRS and the WISPER calibration. This is consistent

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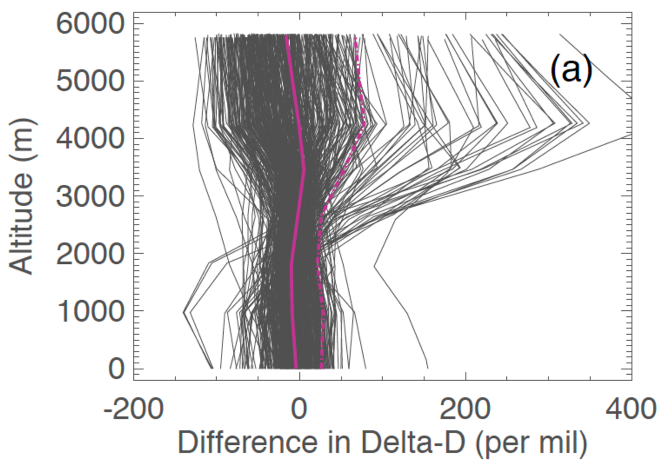
with TES δD (Worden et al., 2019; Herman et al., 2014). AIRS lower-tropospheric δD bias is -6.6‰ and RMS 20.9‰ (surface to 800 hPa). In the mid-troposphere, 800 to 500 hPa, AIRS δD bias is -6.8‰ and RMS 44.9‰.



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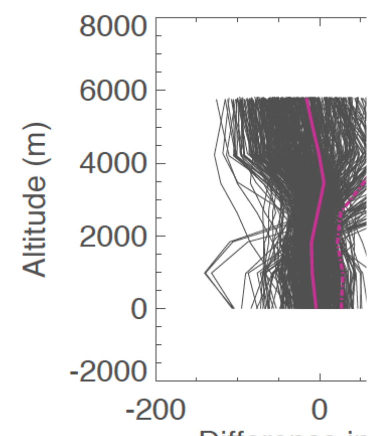

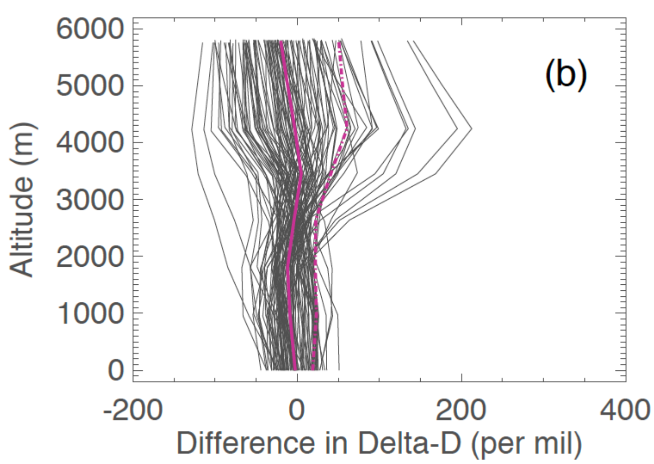

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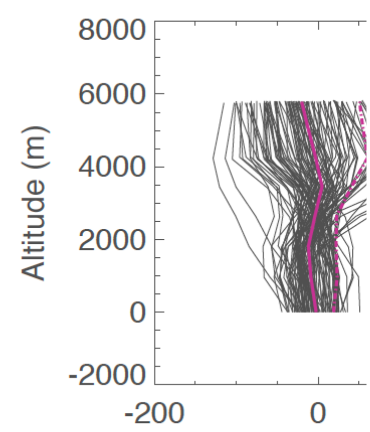

Figure 4. (a) AIRS minus ORACLES aircraft δD for the 446 matches within the loose spatial matching constraint (Fig. 2 open circles). Lines are individual profiles (black lines), mean (red solid line) and RMS (red dash dot line).

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(b) AIRS minus ORACLES aircraft δD for the 110 matches within 0.3 degrees (Fig. 2 closed circles).

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Table 2. Summary of satellite-aircraft comparisons for 110 matched pairs in 2016 (Fig. 2 closed circles). Bias and RMS (standard deviation) of AIRS δD relative to ORACLE aircraft with averaging kernel applied ("BiasAK", "RMSak"), and for AIRS relative to mapped ORACLES aircraft, no averaging kernel ("Bias", "RMS"). The reported RMS here is the standard deviation, not including the bias.

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Altitude (m)	Pressure (hPa)	BiasAK (‰)	RMSak (‰)	Bias (‰)	RMS (‰)
0.01	1014.63	-2.46	18.98	-14.82	22.64
136.61	1000.00	-3.35	19.38	-18.14	22.79
968.87	908.51	-8.86	23.39	-0.31	131.50
1807.71	825.40	-11.80	22.05	9.77	89.68
2641.34	749.89	-3.89	22.63	-13.24	38.07
3456.36	681.29	4.89	41.03	-3.66	35.98
4250.29	618.97	-2.96	60.63	12.52	76.03
5027.62	562.34	-11.87	55.15	-16.62	73.75
5792.12	510.90	-20.09	50.61	-40.41	81.22

5. Error estimation

In this section we characterize the *a posteriori* error budget for AIRS HDO/H_2O and assess this error by comparison with the ORACLES aircraft measurements. Error analysis in OE has been described in detail in the literature (Worden et al., 2004, 2006; Bowman

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et al., 2004; Rodgers, 2000). The error $\boldsymbol{x}$ in the estimate of HDO/H_2O is defined as the true state $\boldsymbol{x}$ minus the linear estimate $\boldsymbol{x}$ retrieved by AIRS (e.g., Worden et al., 2006, Eq. (15)):

$$\boldsymbol{x} = \boldsymbol{x} - \boldsymbol{x}. \qquad (3)$$

Similar to Herman et al. (2014), we define the *estimated error* of the AIRS isotopic ratio HDO/H_2O, (Eq. 4) as the observation error covariance (Worden et al., 2006):

$$\boldsymbol{S} = \boldsymbol{G_R S_n G_R^T} + \boldsymbol{G_R}\left(\sum_i \boldsymbol{K_i S_b^i K_i^T}\right)\boldsymbol{G_R^T}, \qquad (4)$$

where $\boldsymbol{G_R} = (\boldsymbol{G_z^D} - \boldsymbol{G_z^H})$ is the gain matrix of the HDO/H_2O retrieval, $\boldsymbol{S_n}$ is the measurement error covariance, and $\boldsymbol{S_b^i}$ is the error covariance due to systematic errors and interference errors. Interference errors are due to CH_4, N_2O, surface emissivity, effects of temperature, and clouds. The estimated error is given by the square roots of the diagonal elements of $\boldsymbol{S}$, the best estimate of the AIRS observation error covariance for the HDO/H_2O retrieval.

The estimated error (Eq. 4) is compared to the empirical error calculated from the AIRS-aircraft comparisons. It is seen that the error varies from ~20 to ~40 per mil (Fig. 5). The empirical error (AIRS versus aircraft RMS) is similar in magnitude to the estimated error, but exceeds the estimated error at 500 to 600 hPa in the free troposphere. These differences between the OE estimated error and the empirical error are likely due to uncertainties in atmospheric variability in space and time and in the collocation between satellite retrieval and aircraft measurements. The instrument operator (Eq. 1) accounts for error due to the mismatch in *vertical* sensitivity between the satellite retrieval and aircraft *in situ* vertical profiling. In the cases where AIRS is compared to *in situ*

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measurements without the instrument operator, there is an additional smoothing error (Table 2). The instrument operator does not account for error due to *horizontal* mismatch. The close coincidences are all within 30 km (0.3 degrees), but given time differences, and the AIRS 15-km nadir footprint and limited in situ measurement, the satellite and aircraft are not necessarily measuring the same airmass. There is a collocation error on the order of ~10 per mil due to horizontal collocation/representativeness uncertainty.

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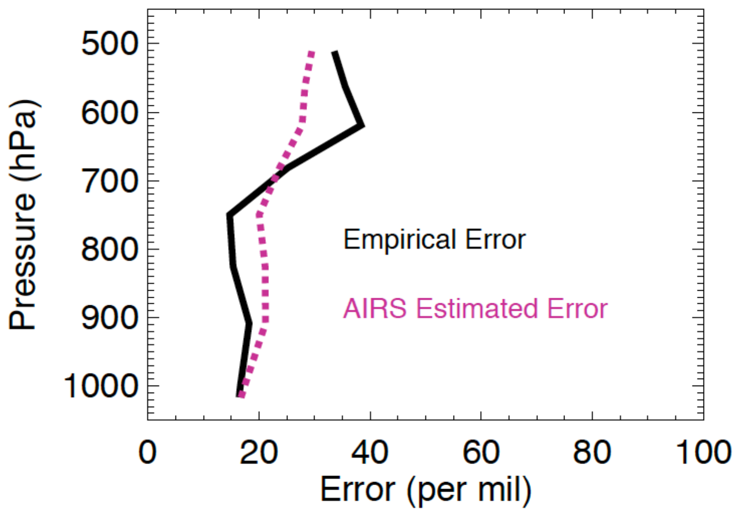

Figure 5. Plot of AIRS error analysis for coincident AIRS and ORACLES δD on 31 August 2016 shows that the empirical error is comparable to the AIRS estimated error. The empirical error is obtained from the statistics of the satellite-aircraft comparison, while the estimated error is obtained from optimal estimation retrieval theory. Plotted here are the AIRS δD estimated error also known as AIRS observation error (red dashed line) and the AIRS δD empirical error (black line).

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6. Conclusions

HDO/H_2O estimates from AIRS single footprint radiances been compared to coincident *in situ* airborne measurements on the P-3B Orion aircraft by the Oregon State Water WISPER system over the Southeast Atlantic Ocean. On eight days between 31 Aug and

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25 Sep 2016, there are collocated measurements between AIRS and the P-3B aircraft. We have shown that AIRS-only retrievals have sensitivity to HDO from the middle troposphere to the lower troposphere. We demonstrate that AIRS δD has a mean bias of -6.7‰ relative to aircraft, well within the estimated measurement uncertainty. In the lower troposphere, 1000 to 800 hPa, AIRS δD bias is -6.6‰ and the RMS 20.9‰, consistent with the calculated uncertainty of 19.1‰. In the mid-troposphere, 800 to 500 hPa, AIRS δD bias is -6.8‰ and RMS 44.9‰, comparable to the calculated uncertainty of 25.8‰. The errors are sufficiently small that the AIRS HDO/H_2O ratio retrievals are useful for scientific analysis. This long term global data record has much potential utility.

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Code/Data availability. The ORACLES aircraft data used in the data analysis can be freely downloaded from the following Digital Object Identifier: (http://dx.doi.org/10.5067/Suborbital/ORACLES/P3/2016_V1, last access: 22 April 2017). We expect the AIRS-based deuterium data to be publicly released by January 2020. Files in IDL format of the AIRS data shown and forward model output are available from coauthor John Worden upon request: john.r.worden@jpl.nasa.gov.

Team list. Robert L. Herman (RH), John Worden (JW), David Noone (DN), Dean Henze (DH), Kevin Bowman (KB), Karen Cady-Pereira (KC), Vivienne H. Payne (VP), Susan S. Kulawik (SK), and Dejian Fu (DF).

Author contribution. RH carried out all steps of aircraft validation, from matching data and quality filtering to applying observation operator and statistics, while JW provided satellite-to-satellite validation. JW developed the retrieval strategies for both AIRS and TES HDO/H_2O retrievals. DF and SK built the strategies of single AIRS footprint HDO/H_2O retrievals into the MUSES algorithm. KC, RH and VP evaluated the sensitivities of retrievals to the choice of forward model. RH, VP, JW, SK, DF, DN, DH and KB contributed to the text and interpretation of the results. JW and SK helped in the estimation of HDO/H_2O measurement uncertainty, quality flagging and knowledge of the retrieval process. DN and DH provided ORACLES data, aircraft measurement uncertainty, and identified profiles in the aircraft data. All authors participated in writing the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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