Ground-based remote sensing of tropospheric HDO/H_2O ratio profiles

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Presentation and validation of an innovative retrieval approach PROFFIT (V9.4):

Motivation: Ground-based FTIR allows monitoring of many trace species in the atmosphere. In addition, significant variability in isotopic composition can be measured for several species (e.g. O3, H2O, …). Whereas the retrieval of vertical profiles for individual species has reached a high level of sophistication, codes still lack to support dedicated isotopic retrieval work.

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The additional complication of isotopic retrieval

Target quantity: *ratio* of the isotopic species as function of altitude

Standard approach: the isotopic species are jointly retrieved from a measured spectrum and the resulting profiles are compared.

Drawback: AKs of the two species can differ significantly. So the profiles are incompatible. The situation is equivalent to the case of comparing profiles of a certain species measured by different remote sensing instruments (yes, again Rodgers & Connor …).

How can VMR-ratios be constrained properly?

The advantages of a log-retrieval (Hase et al.,“intercomparison of retrieval codes…“, JQSRT, 2004):

- exclude unreasonable (negative) VMRs
- log-normal pdf is superior guess in case of large percentage variability.

These claims have been proven for H_2O profile retrievals by careful intercomparison of Izaña FTIR results with sonde data (Schneider et al. ,“water vapour profiles by ground-based FTIR…“, ACP, 2006).

OE / TP methods constrain differences between components of the solution vector and the a-priori vector. *Differences between log(VMR) components correspond to ratios of the VMR quantities*:

$$\log(a / b) = \log(a) - \log(b)$$

In the following the possibilities of the PROFFIT Ver. 9.4 isotope retrieval option will be presented:

- Theoretical estimation of precision of HDO/H2O ratios (common approach versus PROFFIT Ver. 9.4)
- Empirical validation and interpretation of HDO/H2O ratios retrieved from spectra measured at Izaña

The theoretical error estimation is performed in form of a full treatment (reason: important non-linearities):

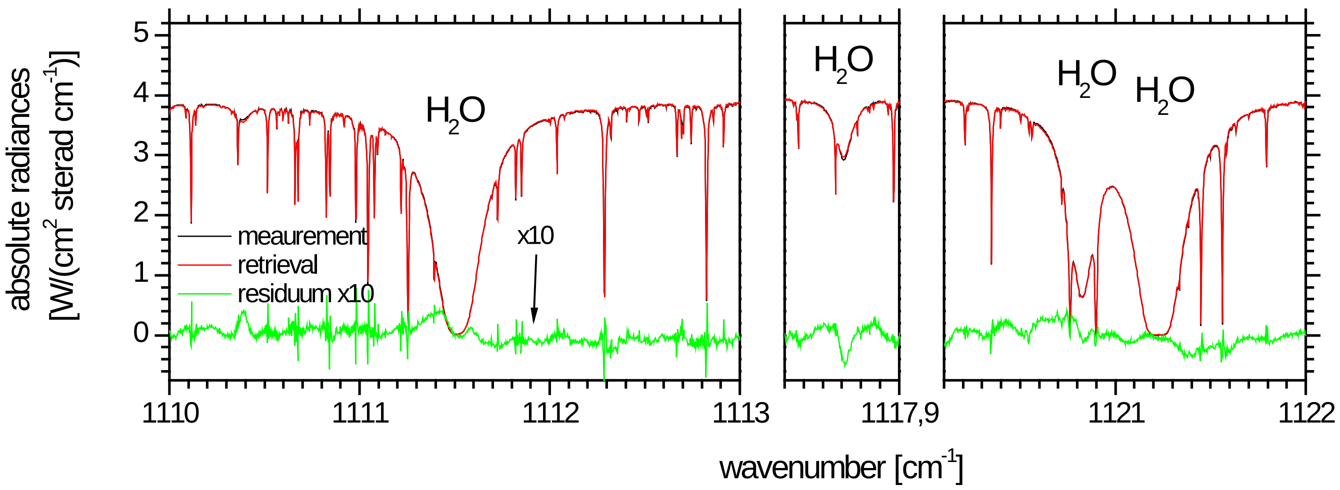
1. Forward calculation of assumed HDO and H_2O profile pairs

2. Introducing of errors (measurement noise, temperature profile, ILS, spectroscopic parameter, …)

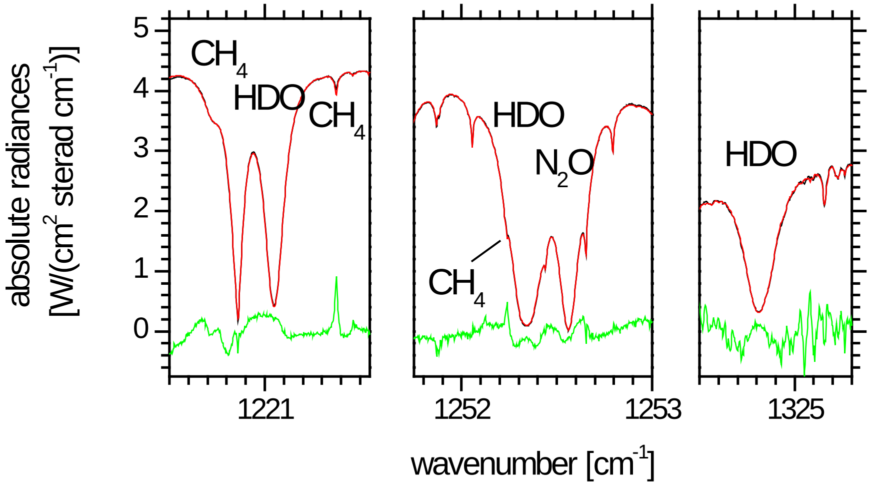
3. Inversion of the simulated spectra

This „Monte Carlo“ error estimation works only if we apply a large ensemble of HDO and H_2O profile pairs, which obey the real HDO/H_2O statistics !

Applied spectroscopic windows:



H_2O



HDO

Detection of atmospheric δD variabilities:

The problem:

δD variabilities are very small (σ of 7%, compared to σ of H_2O or HDO of 100%) → measurements have to be very precise !

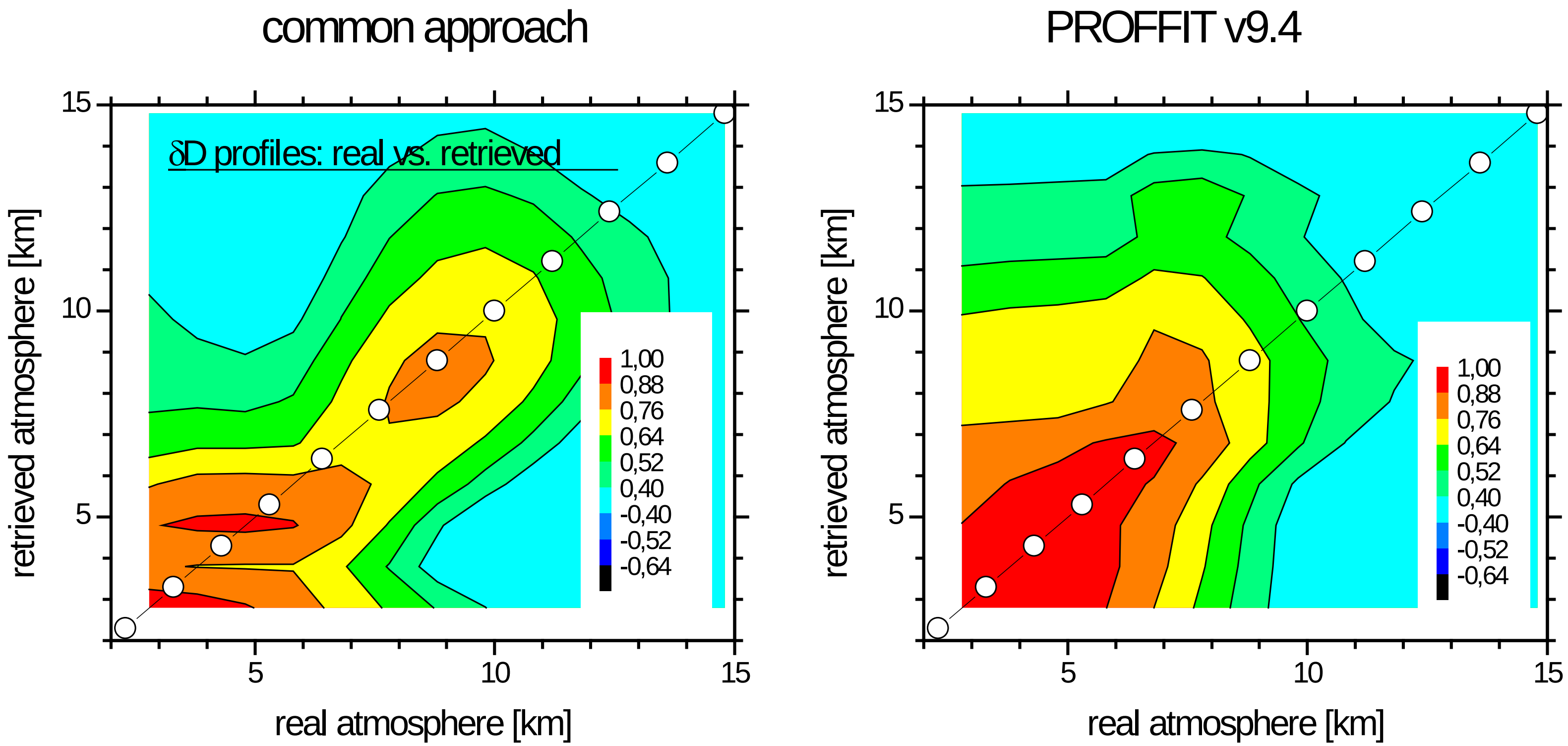
Advantage:

HDO and H_2O have some errors in common → these errors are eliminated when calculating the ratio.

Here we examine if a common approach (individual OE of HDO and H_2O and subsequent calculation of the ratio) already provides for a satisfactory precision, or if the PROFFIT Ver. 9.4 isotope retrieval option (OE of the ratio itself) has to be applied.

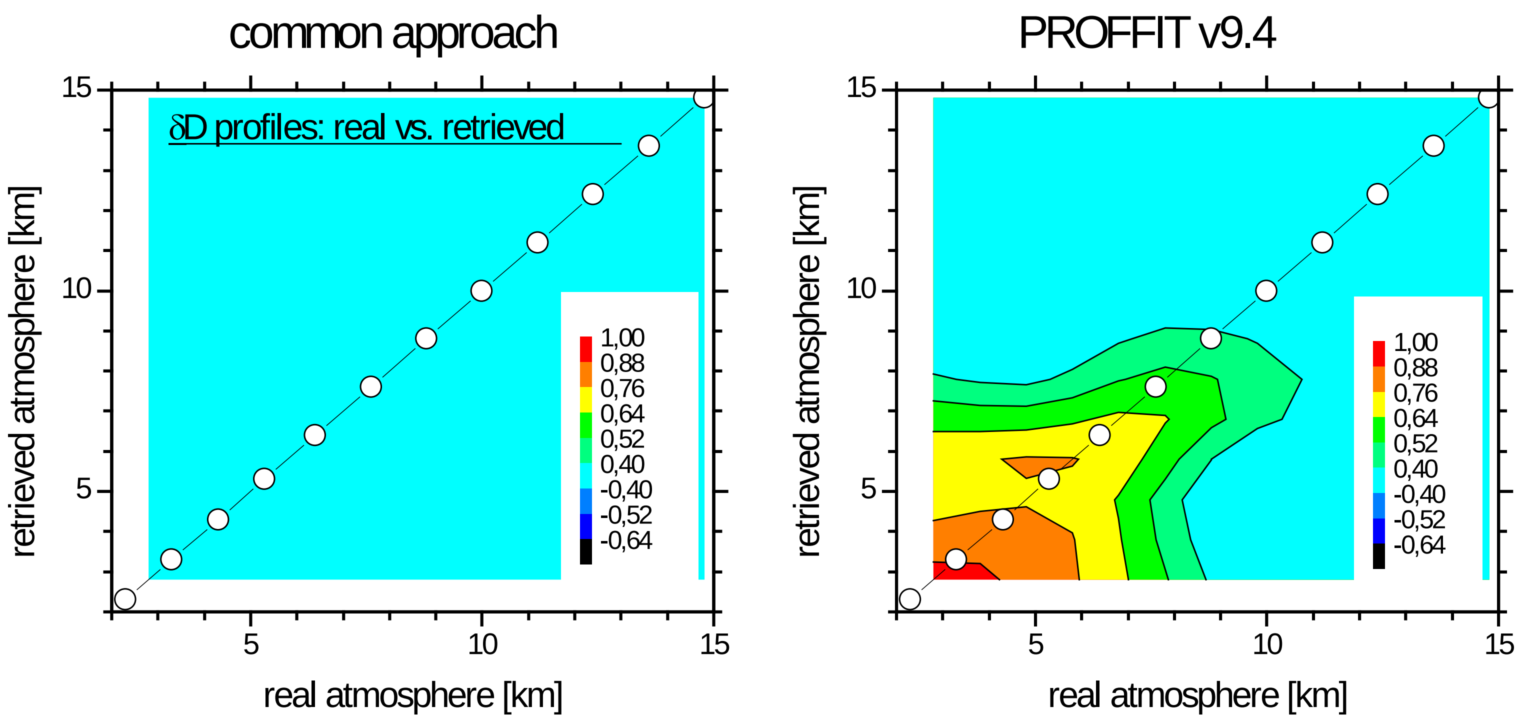
Smoothing error

Correlation between real profiles and retrieved profiles in the absence of measurement noise and parameter errors:



Total error

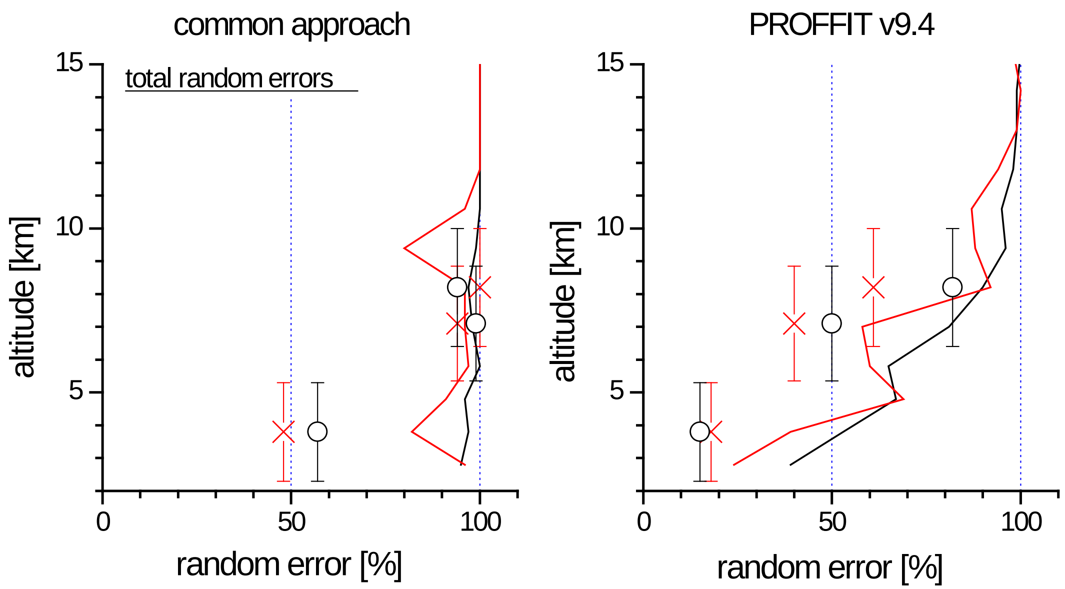
Correlation between real profiles and retrieved profiles for a realistic error scenario:



Theoretical random error estimation (summary)

error source	total column	2.3-4.3km	5.3-8.3km	6.4-10.0km
smoothing	2 (2)	4 (8)	31 (66)	52 (76)
measurement noise	2 (3)	3 (23)	17 (74)	12 (75)
phase error (ILS)	0 (0)	0 (1)	0 (1)	1 (4)
T profile	0 (0)	0 (8)	1 (22)	1 (14)
γ (correlated)	0 (1)	2 (9)	13 (17)	5 (11)
γ (inconsistent)	2 (2)	14 (51)	44 (92)	34 (63)
total	**3 (4)**	**15 (57)**	**50 (99)**	**61 (100)**

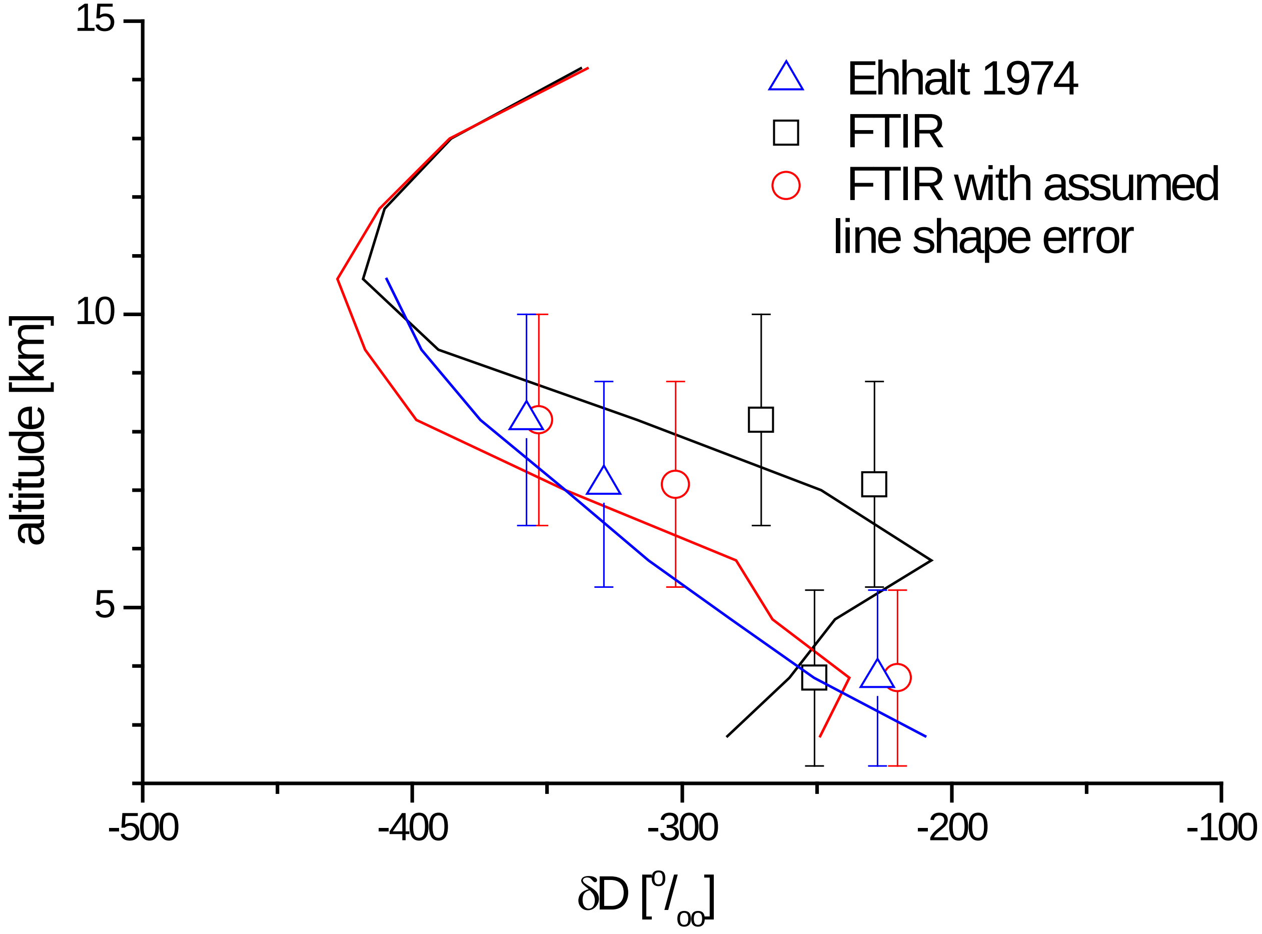
Total error



Precision of common approach only allows us to retrieve the δD variability in the boundary layer.

The PROFFIT Ver. 9.4 isotope retrieval option improves the precision of δD in the boundary layer and enables the retrieval of the δD variability in the middle/upper troposphere.

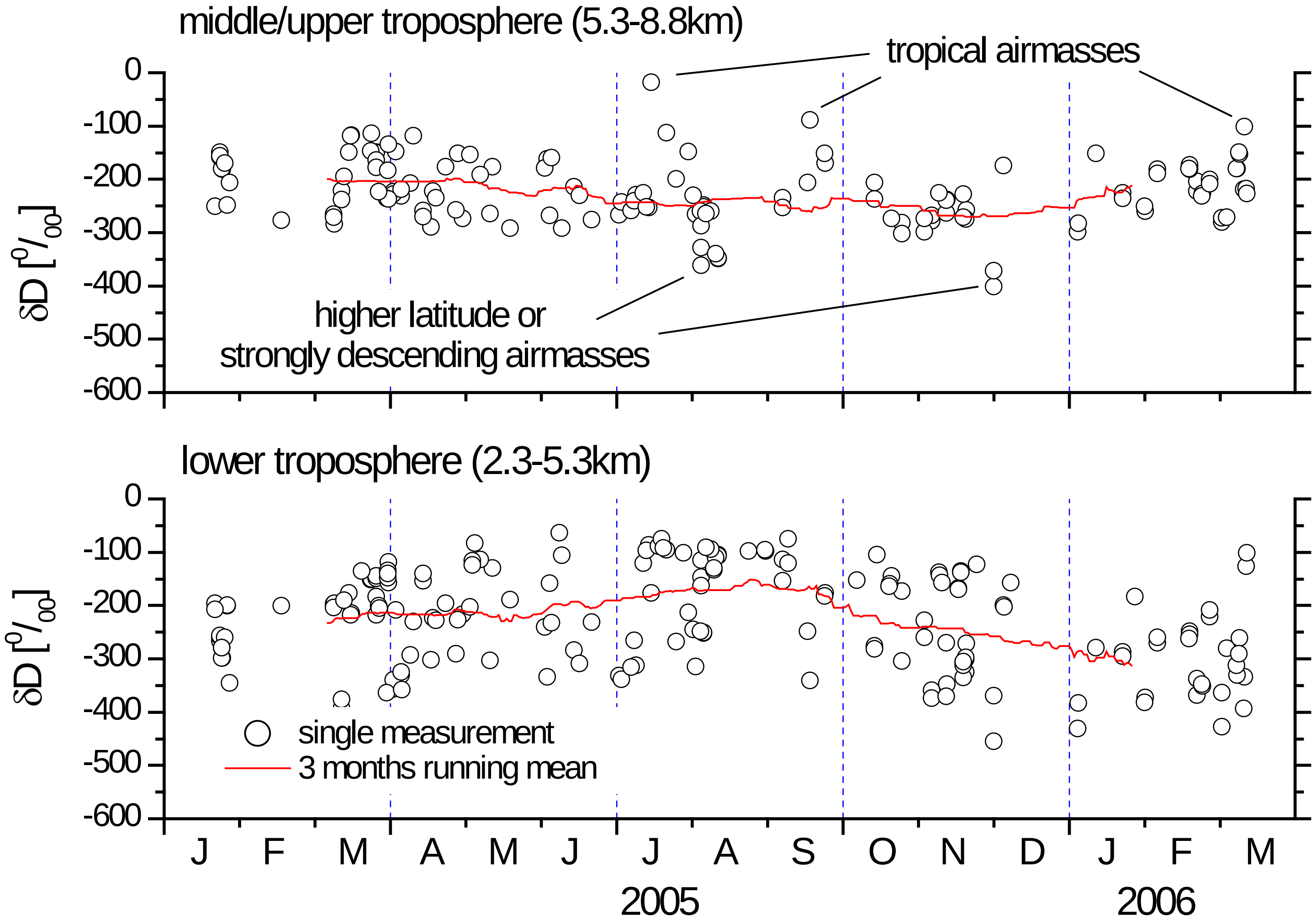
Comparison of mean δD profiles as obtained by Ehhalt (1974) and by our measurements



We find indications of an inconsistency in the line shape of HDO and H_2O !

→ improving the quality of the spectroscopic data would further improve the precision of the retrieved δD values

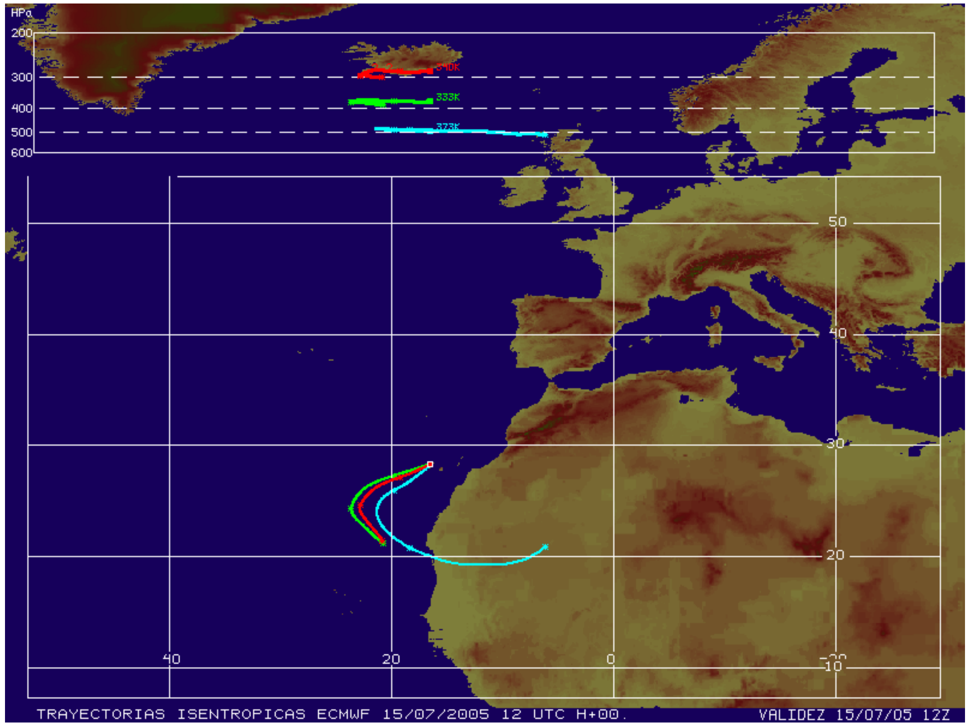
Remote sensing of water vapour isotope ratios above Izaña Observatory:

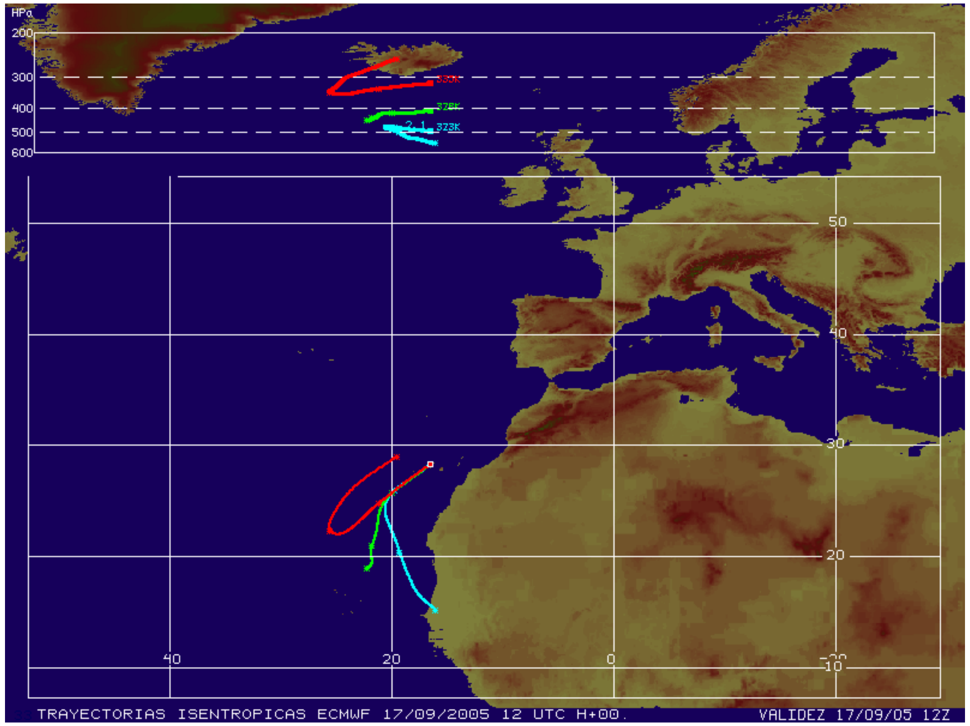


middle/upper tropospheric δD is a good tracer for origin of airmass

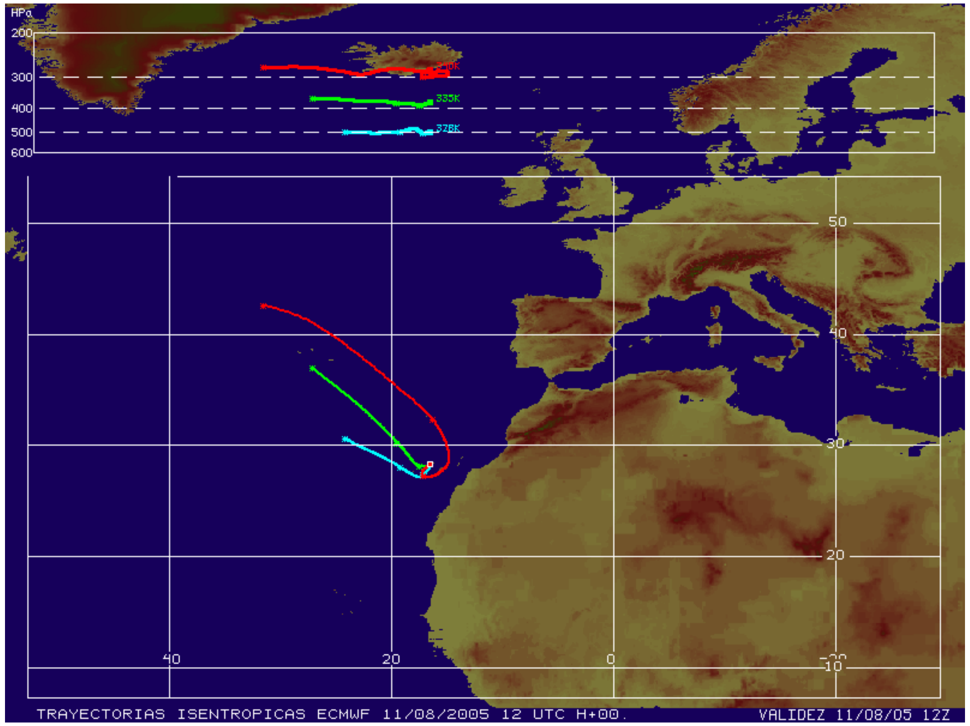
annual cycle in lower troposphere is correlated to sea surface temperature

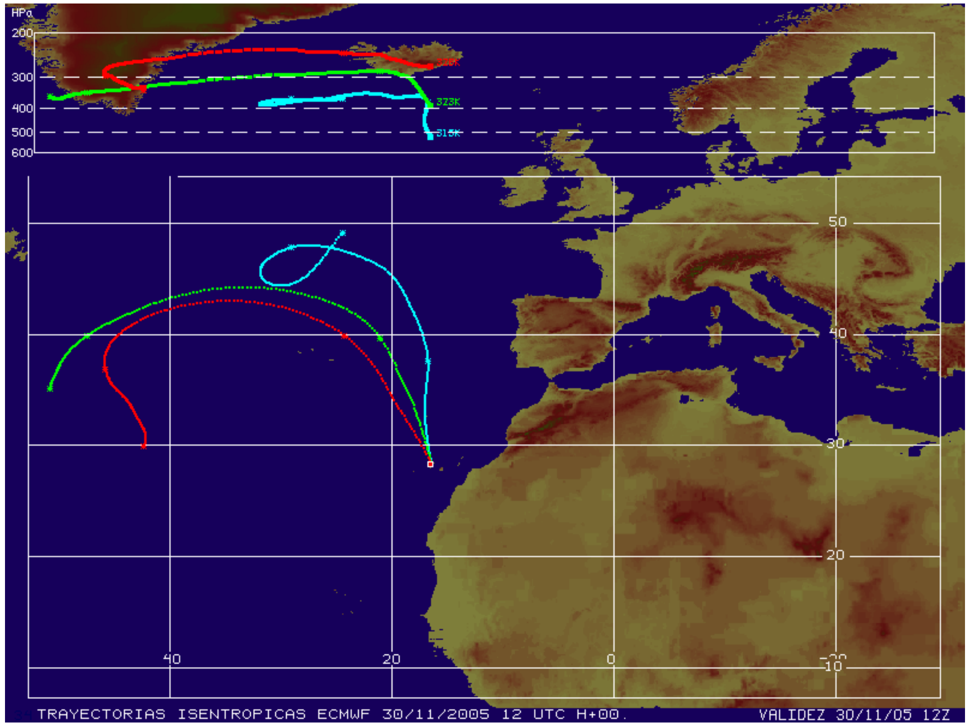
Middle/upper tropospheric trajectories for 15th July and 17th September 2005:



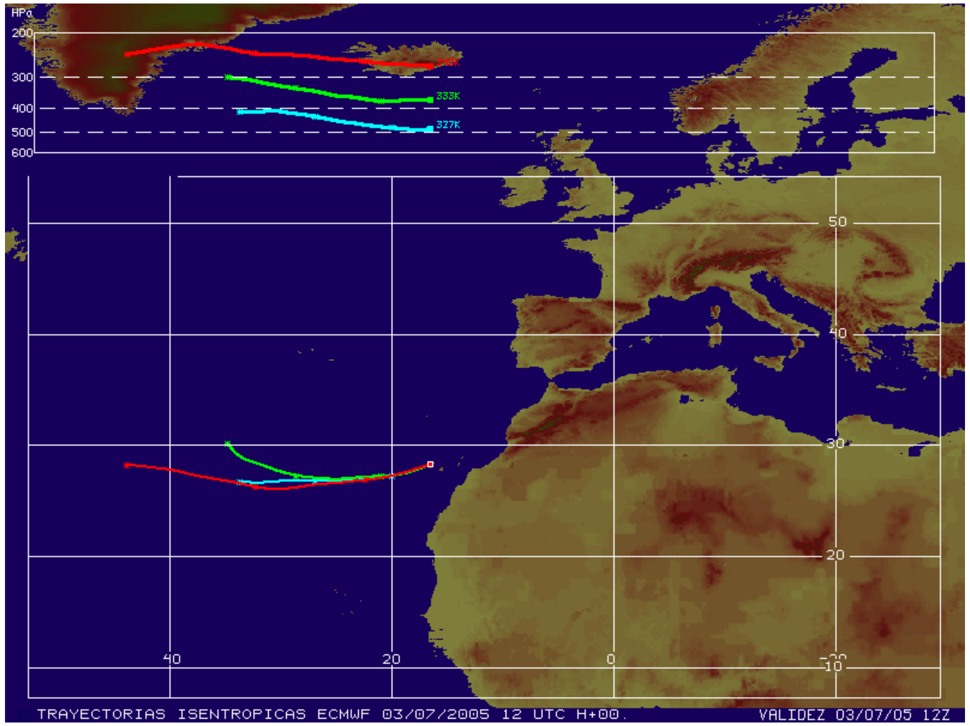


Middle/upper tropospheric trajectories for 10th August and 30th November 2005:





Typical middle/upper tropospheric trajectories (3rd July 2005):

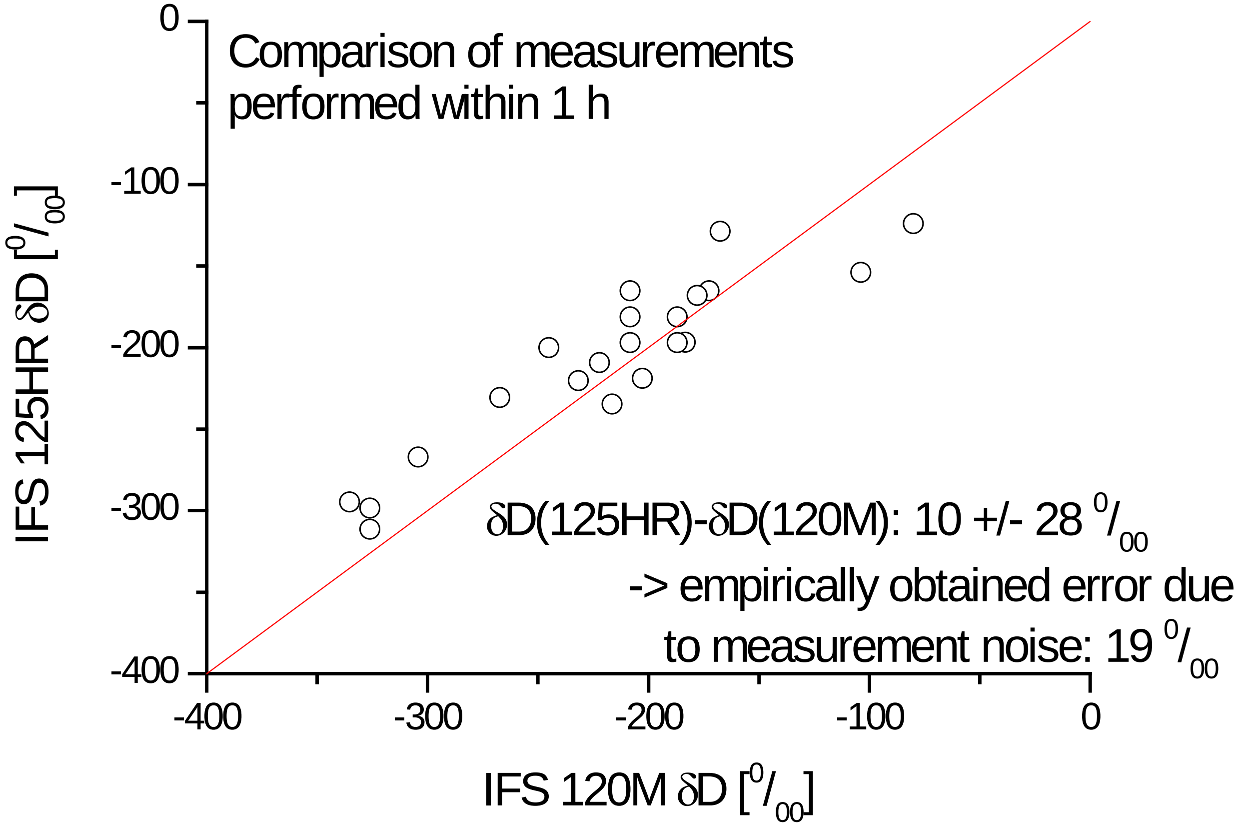


Conclusion of validation:

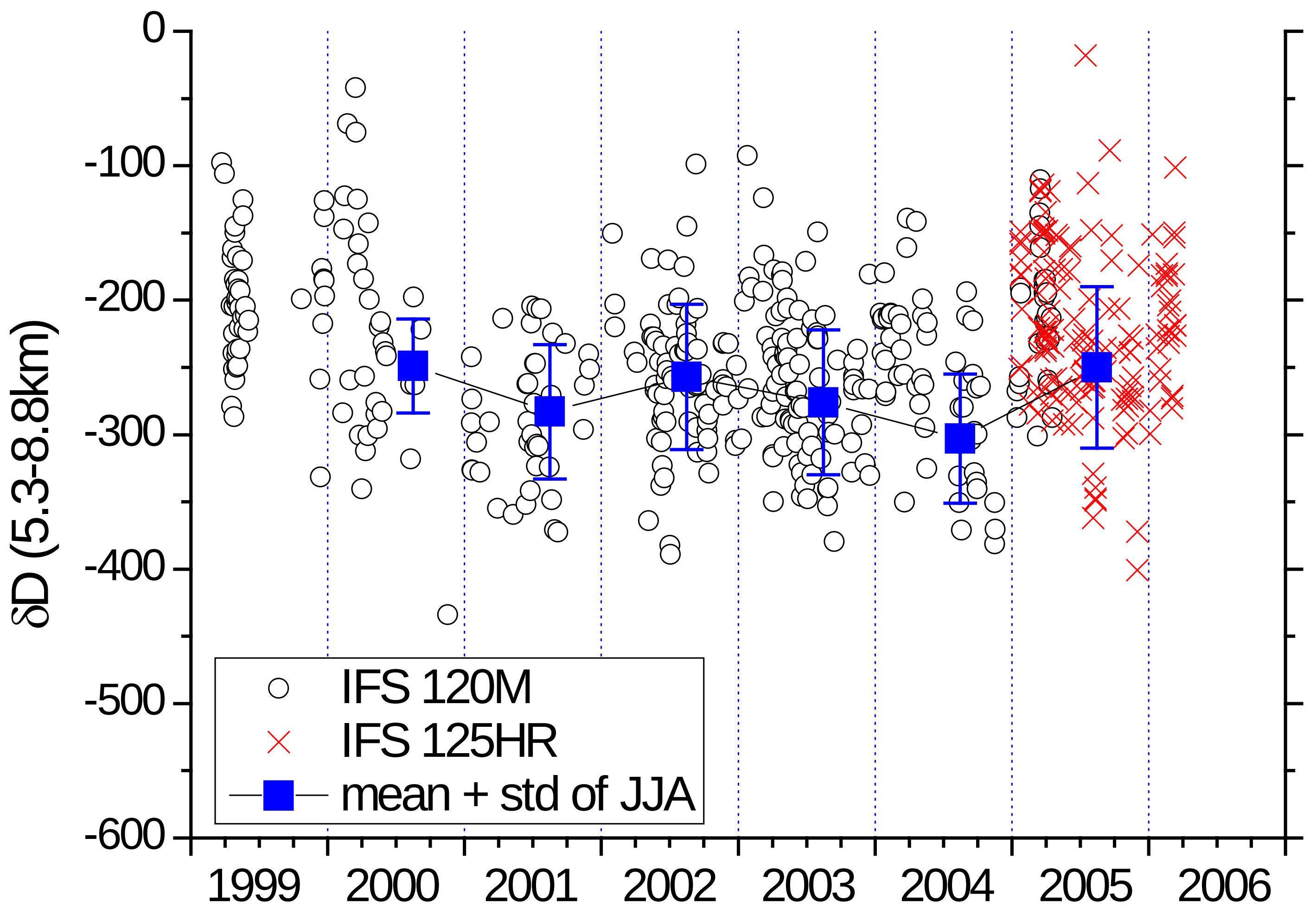
1. The PROFFIT Ver. 9.4 isotope retrieval option yields middle/upper tropospheric δD values with a precision of 50%
2. Middle/upper tropospheric δD gives us information about the static stability of the atmosphere where the airmass comes from (see also Gedzelman, 1988)

Consistency for measurements performed side-by-side with two different FTIR spectrometer:

for the middle/upper troposphere (5.3-8.8km)



7 year time series of middle/upper tropospheric δD in the subtropical eastern Atlantic:



Summary and outlook:

- PROFFIT Ver. 9.4 isotope retrieval option allows for the detection of middle/upper tropospheric δD (common approach doesn’t) !

- Middle tropospheric δD can also be retrieved from lower situated sites (not limited to mountain observatories)

- Method has a wide range of application: isotope ratios for O_3, CH_4, CO_2 (among others); adaptation to satellite codes

- still to do: detailed interpretation of δD time series:

  middle tropospheric δD as index for low static stability in the troposphere, correlation with NAO, ENSO ?

Thank You !!!!!

The additional complication of isotopic retrieval

Possible practical approaches:

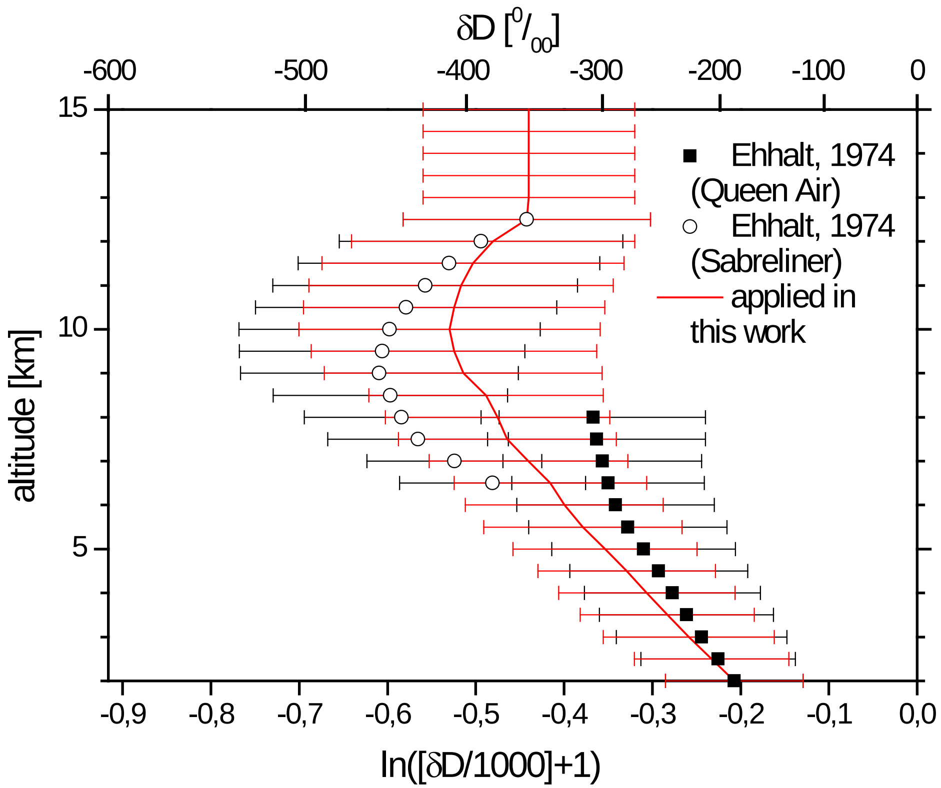
- Accept profiles as given, apply full intercomparison formalism when comparing deduced ratios to model predictions.
  Elaborate post processing, no stand-alone FTIR data product!

- Iterative scheme: main isotope result serves as a-priori for the others.
  Scatter in ratios is reduced, but no reliable scheme, as main isotope AKs imprinted on updated a-priori. Only partial back propagation of the full solution state to the main isotope!
  (Forget about cycling back and forth: beware of “Rodgers trap”)

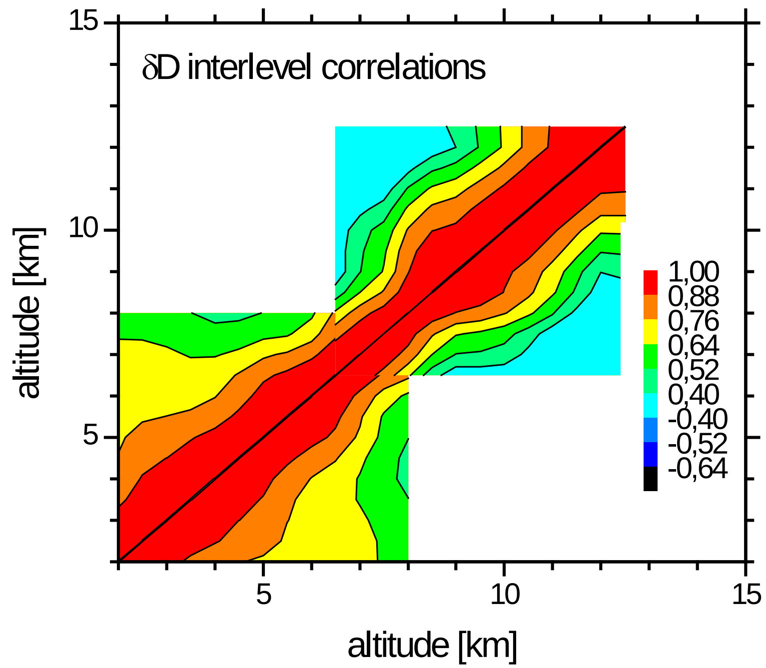
- Optimal scheme: Retrieve the full solution state, add expected correlation between isotopes as additional constraint!
  Individual sensitivities of the isotopes are fully exploited in construction of the full solution state, OE solution for ratio results!

Measurements of HDO/H_2O ratios are rare. Most extensive dataset is from Ehhalt (1974):

median δD profile:



inter-level correlation of δD values:

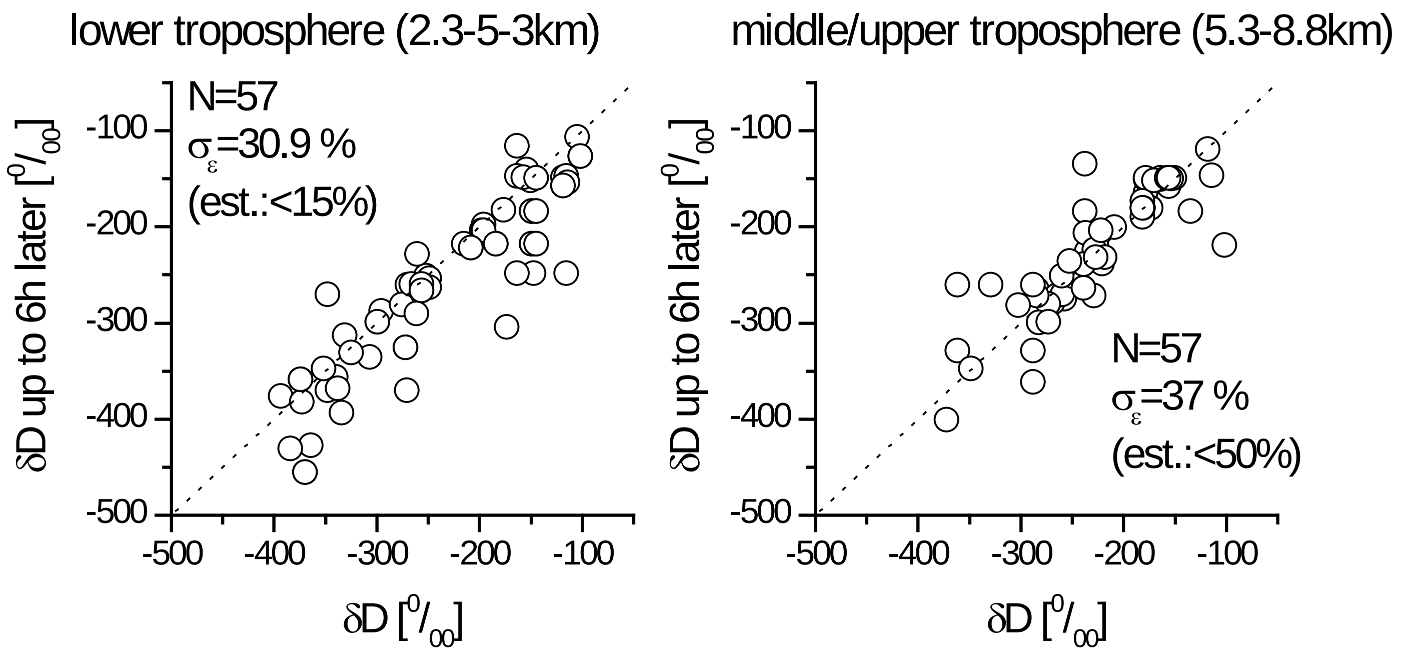


→ we derive HDO/H_2O statistics from Ehhalt (1974) measurements and simulate an ensemble of 500 profile pairs

HDO/H_2O ratio is commonly expressed in form of δD, which is the relative difference of the actual HDO/H_2O ratio to a standard ratio (R_s= 3.1152 x 10^{-4}):

$$\delta D = 1000 \times \left(\frac{[HDO]/H_2O]}{R_s} - 1 \right)$$

Consistency for measurements performed within 6h

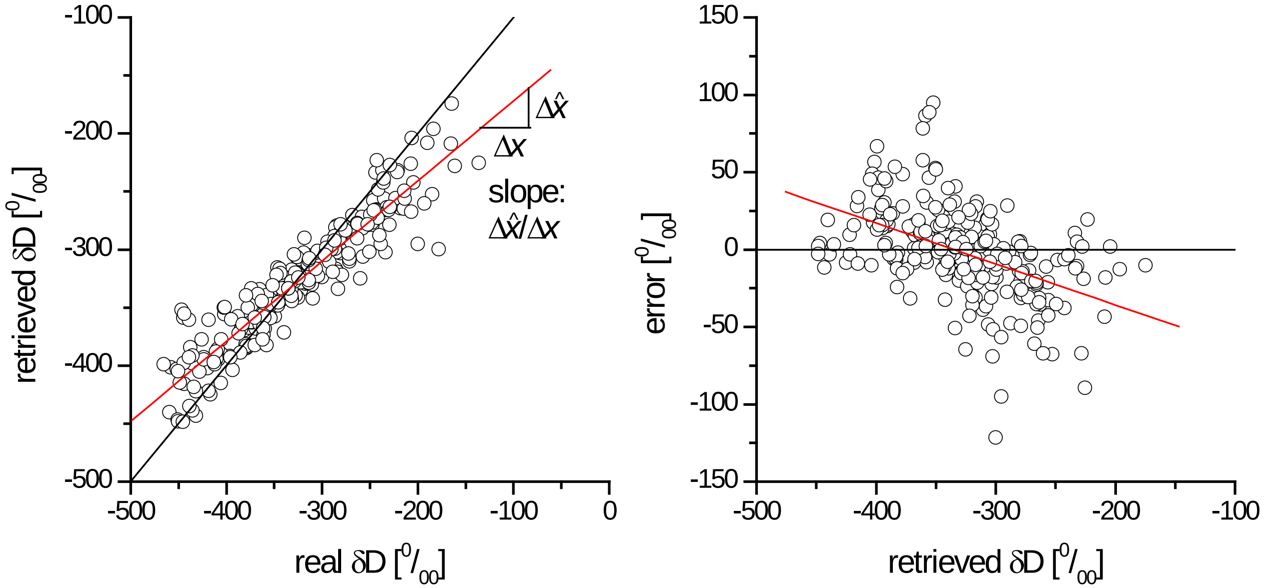


A pair of measurements performed within several hours is only partly representative for the highly variable atmospheric conditions encountered on different days or months. This consistency check should underestimate the overall precision.

lower troposphere: 31% precision → in disagreement with theoretical estimation of 15% !
Reason: in boundary layer exist large variabilities of δD on small time scales

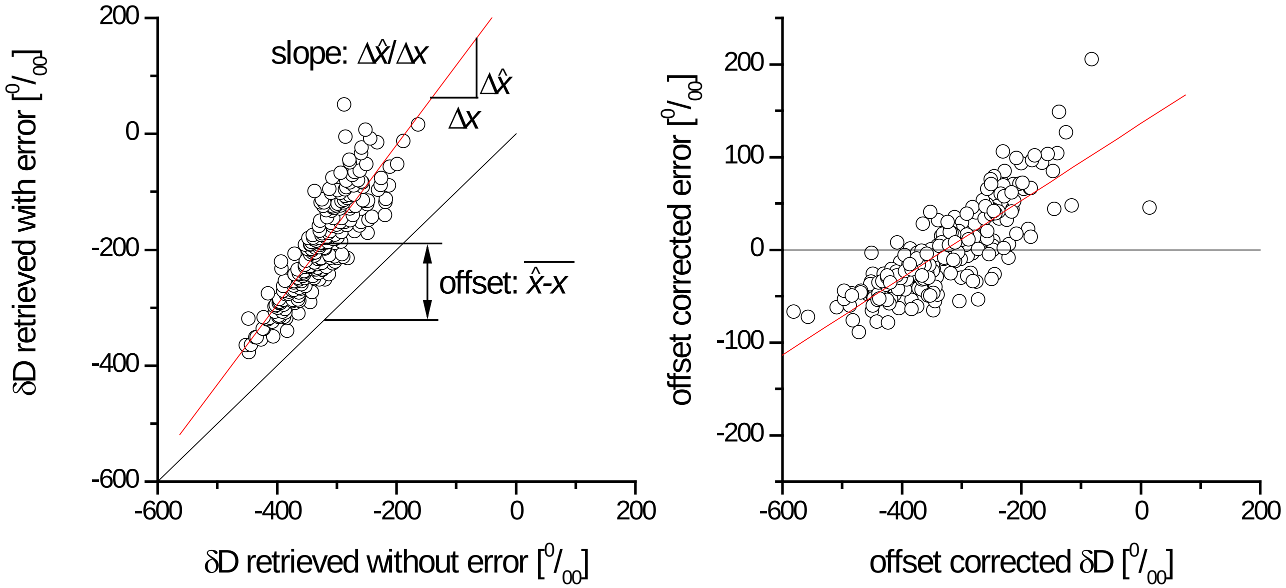
middle/upper troposphere: 37% precision → in agreement with theoretical estimation of 50%

Error estimation by means of linear least squares fit



Smoothing error:

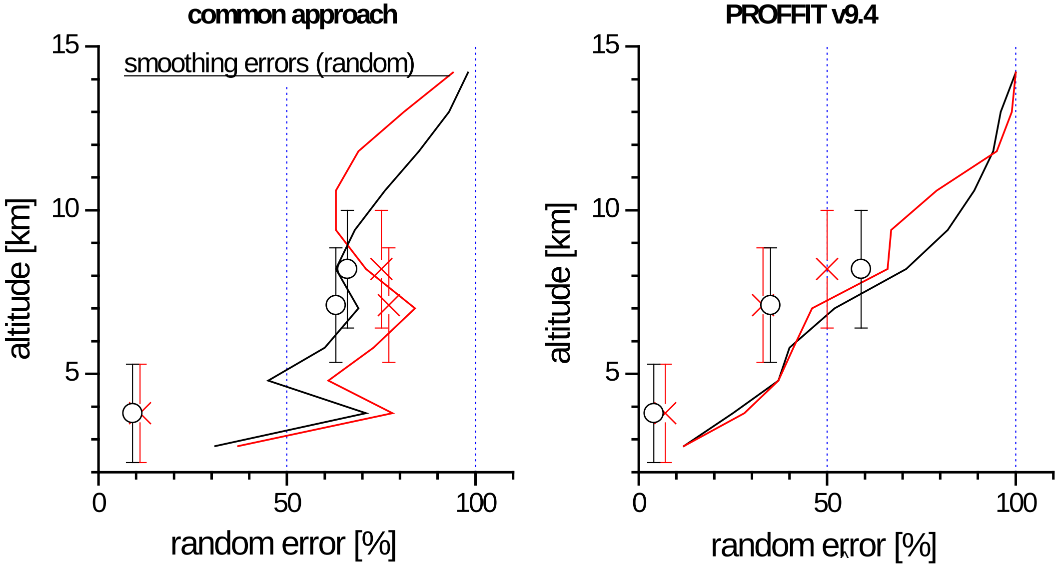
no mean error (no offset) → no systematic error ?
No ! Systematic sensitivity error (slope of regression line < 1) !



Spectroscopic pressure broadening coefficient error:

mean and systematic error

Smoothing error

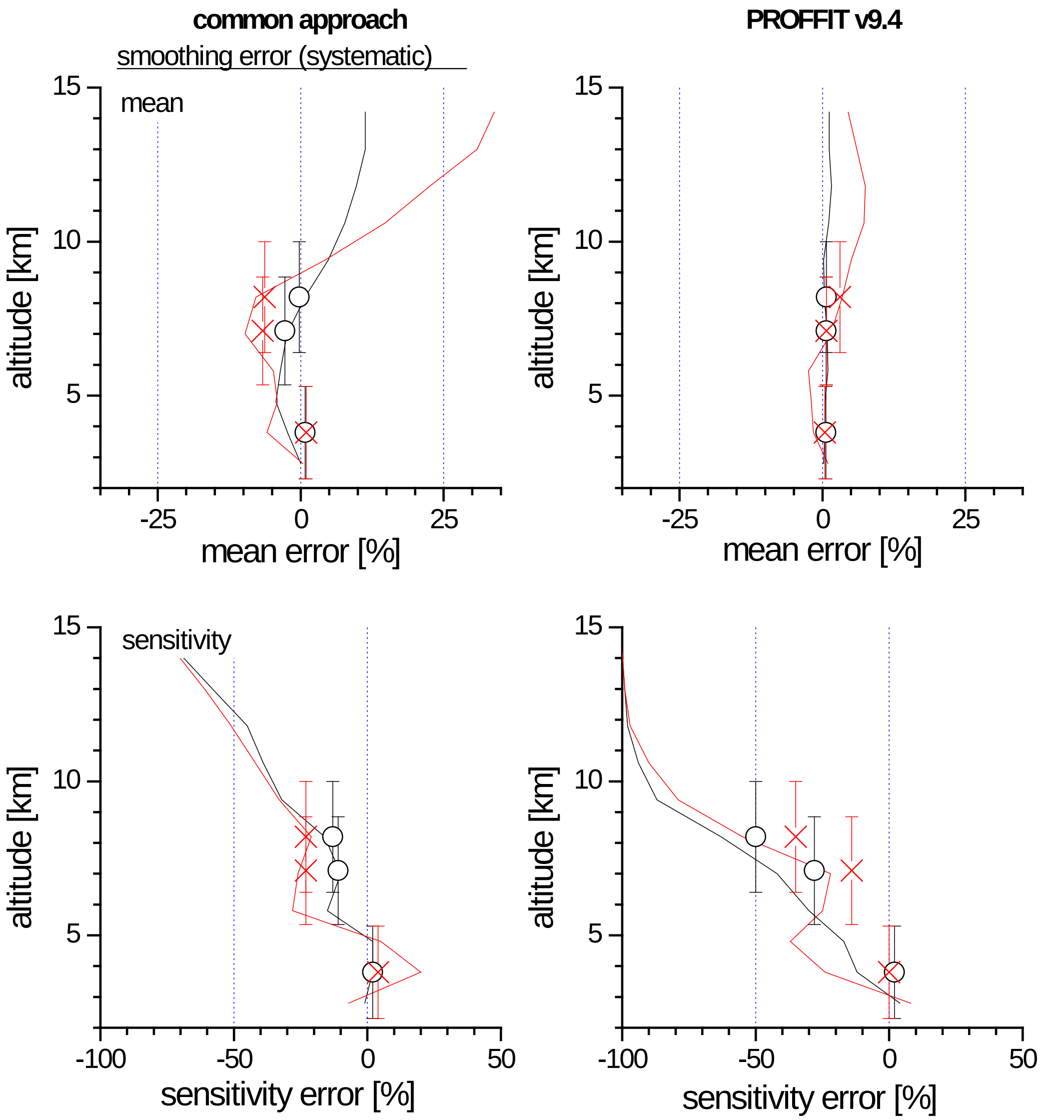


Errors are estimated by least squares fits between real and retrieved δD:

random error component: scattering around the regression curve:

$$\frac{\sigma_{\varepsilon\_reg}}{\sigma_{\hat{x}}} = \sqrt{1-\rho^2}$$

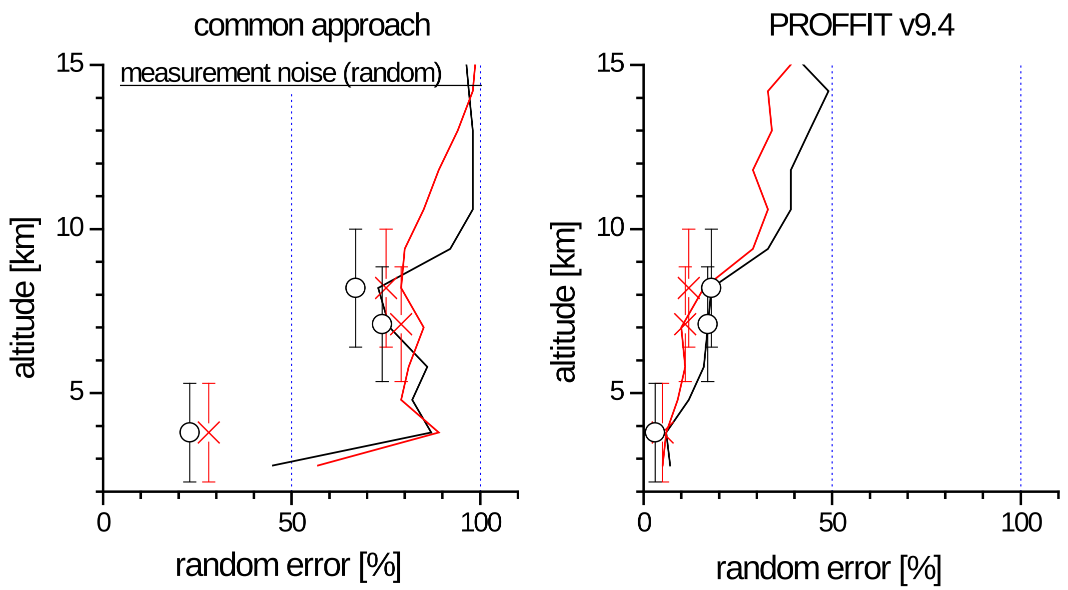
Smoothing error



systematic error component:

difference of regression curve from diagonal: offset (mean error) and slope (sensitivity error)

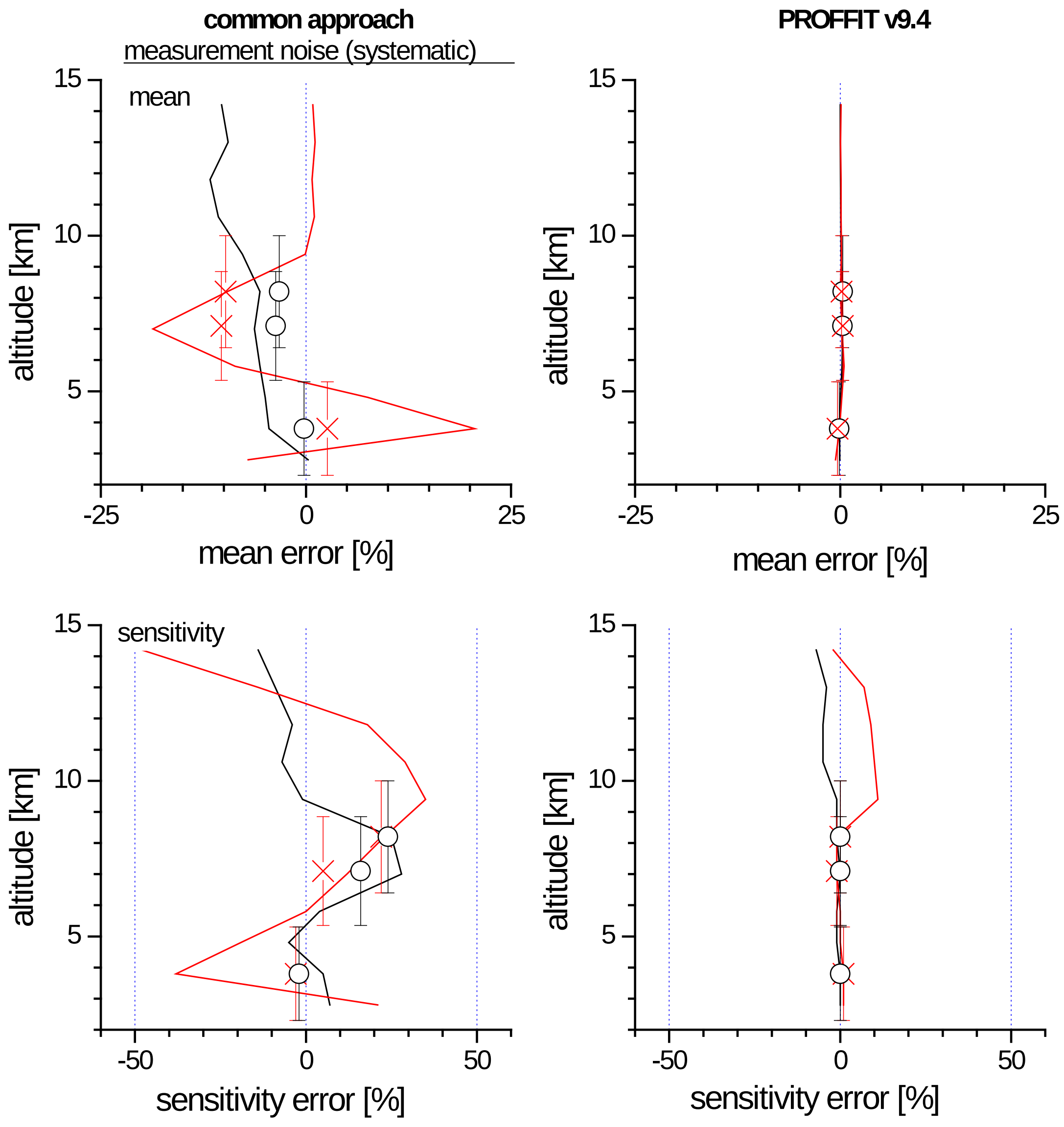
Measurement noise error



This error is not common for HDO and H_2O → error is not eliminated in the ratio when common retrieval is applied

Inter-species constraint forces common response of HDO and H_2O → reduced error in the ratio

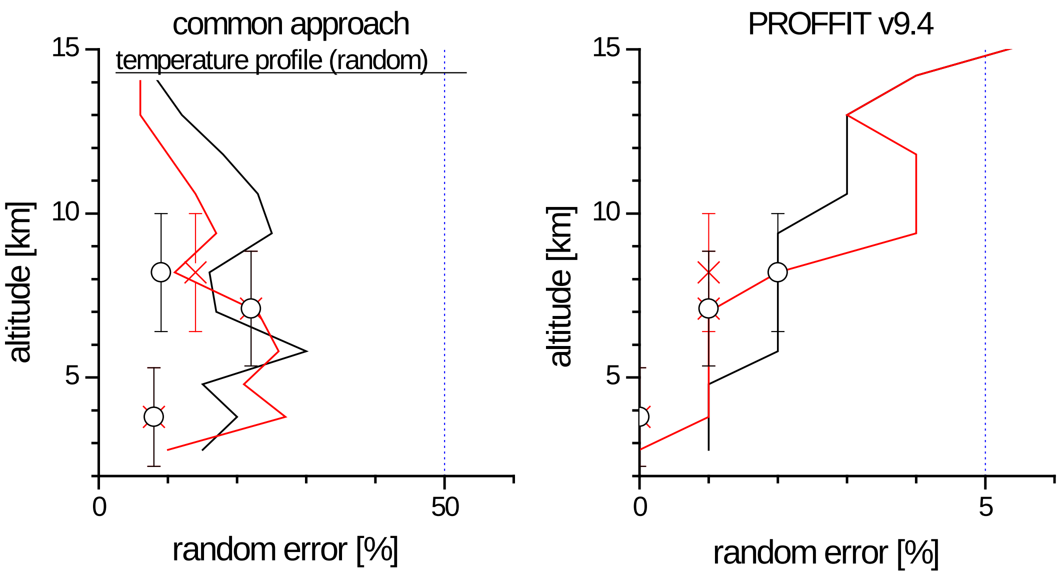
Measurement noise error



Common approach no OE of δD → random error source produces systematic error!

PROFFIT isotope retrieval option provides for OE of δD → random error source produces only random errors

Temperature error

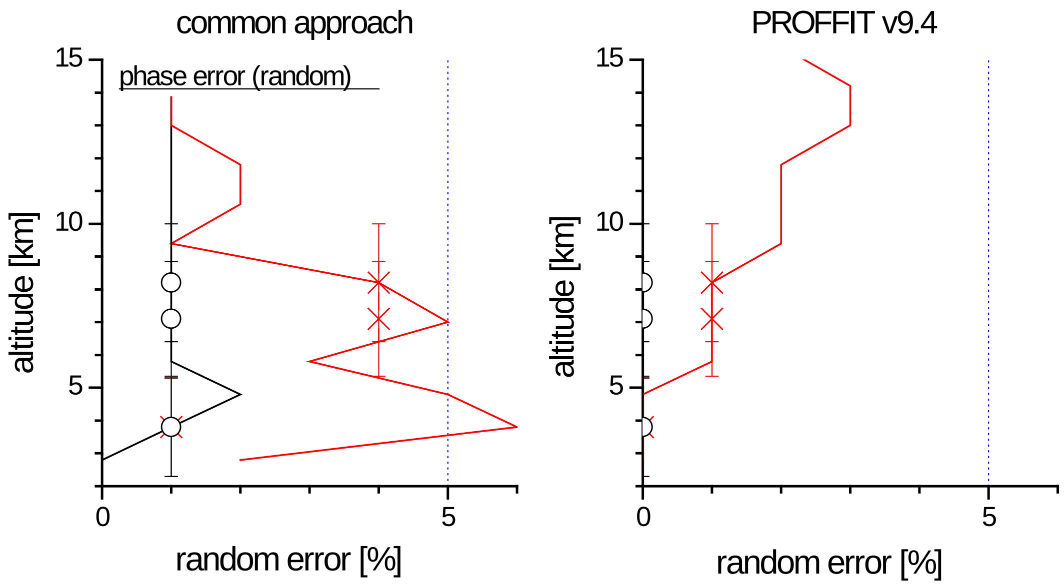


Error in HDO and H_2O similar → already in common approach δD error below 25%

Isotope retrieval option further equalises error responses of HDO and H_2O → very small error in δD

Systematic error of the common approach below 5%

ILS (instrumental line shape) error

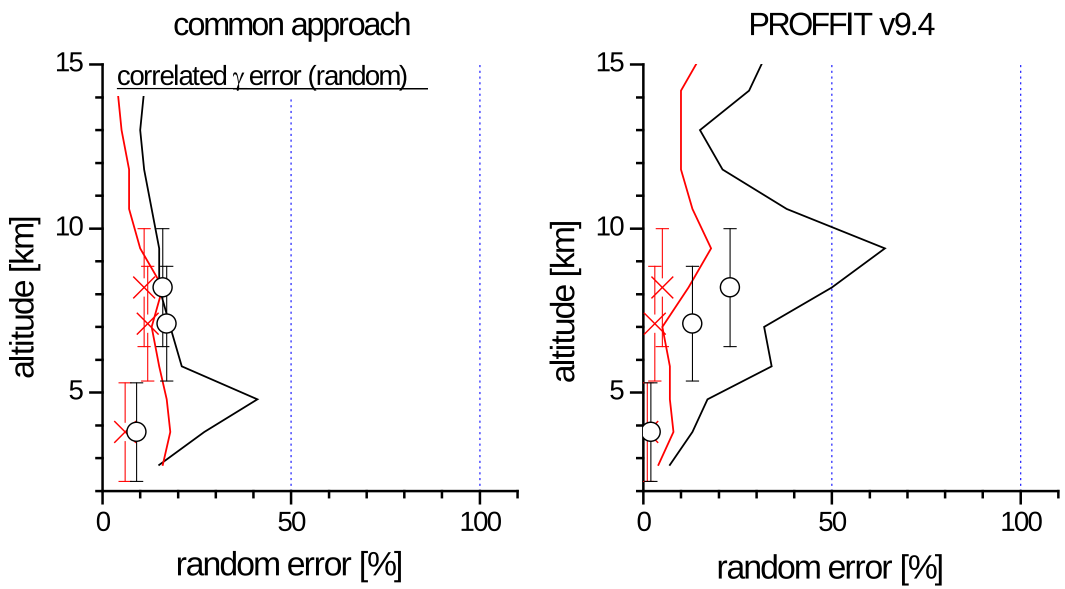


Error in HDO and H_2O common → already in common approach negligible δD error

Isotope retrieval option further equalises error responses of HDO and H_2O → even smaller error in δD

Systematic error of the common approach below 1%

Correlated errors of line shape of H_2O and HDO



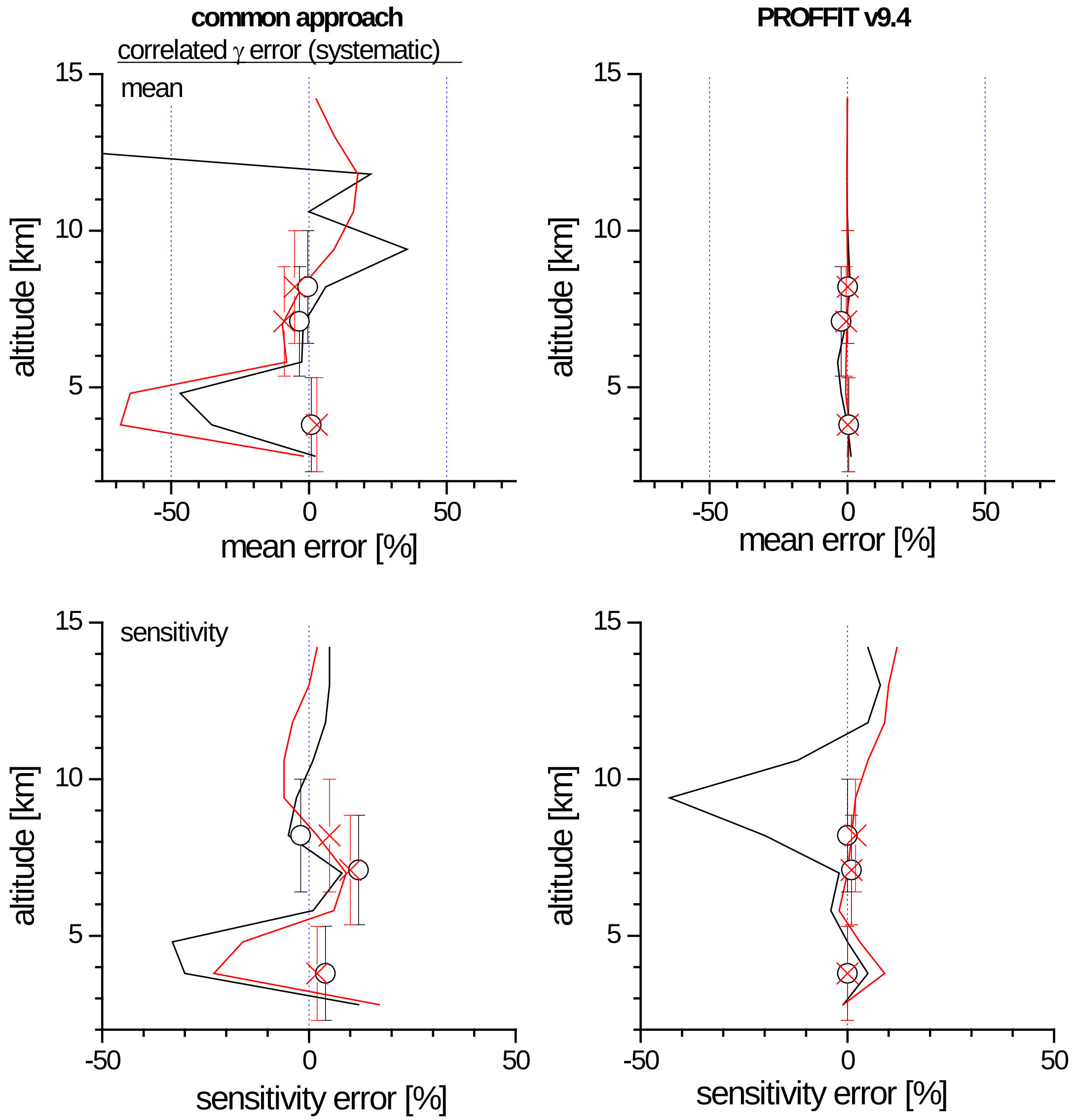
This systematic error source leads to random errors in δD due to non-linearities.

The error source is common for HDO and H_2O, but HDO and H_2O lines have different sensitivities, responses → error is not completely eliminated in ratio when common retrieval is applied

Inter-species constraint forces common response of HDO and H_2O → reduced δD error for unsaturated H_2O lines

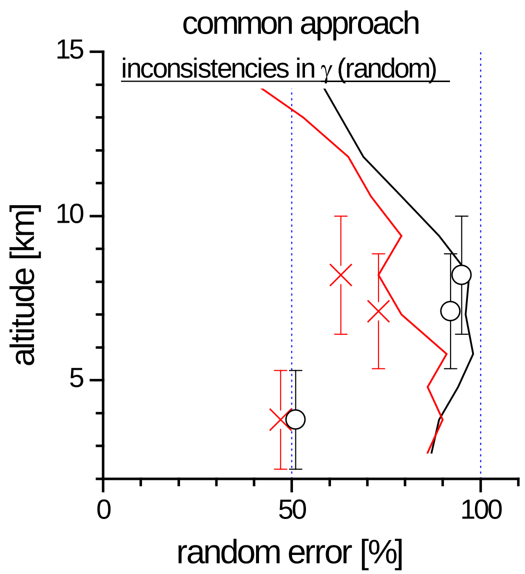
For saturated lines sensitivities of HDO and H_2O are too different → also large error when inter-species constraint is applied

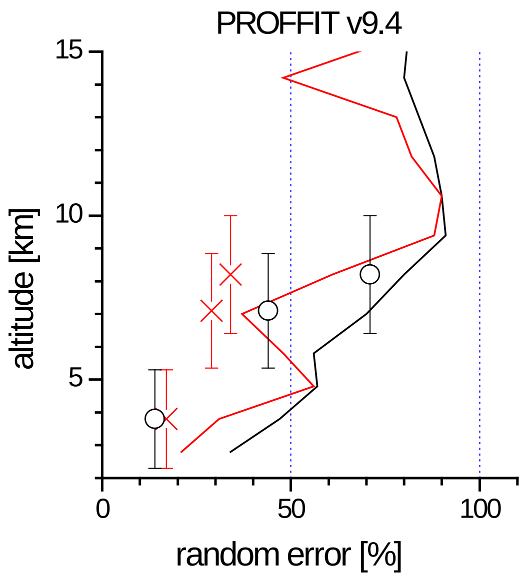
Correlated errors of line shape of H_2O and HDO



Systematic errors are larger for common approach

Inconsistency in line shape of H_2O and HDO (γ(HDO) 2% increased)



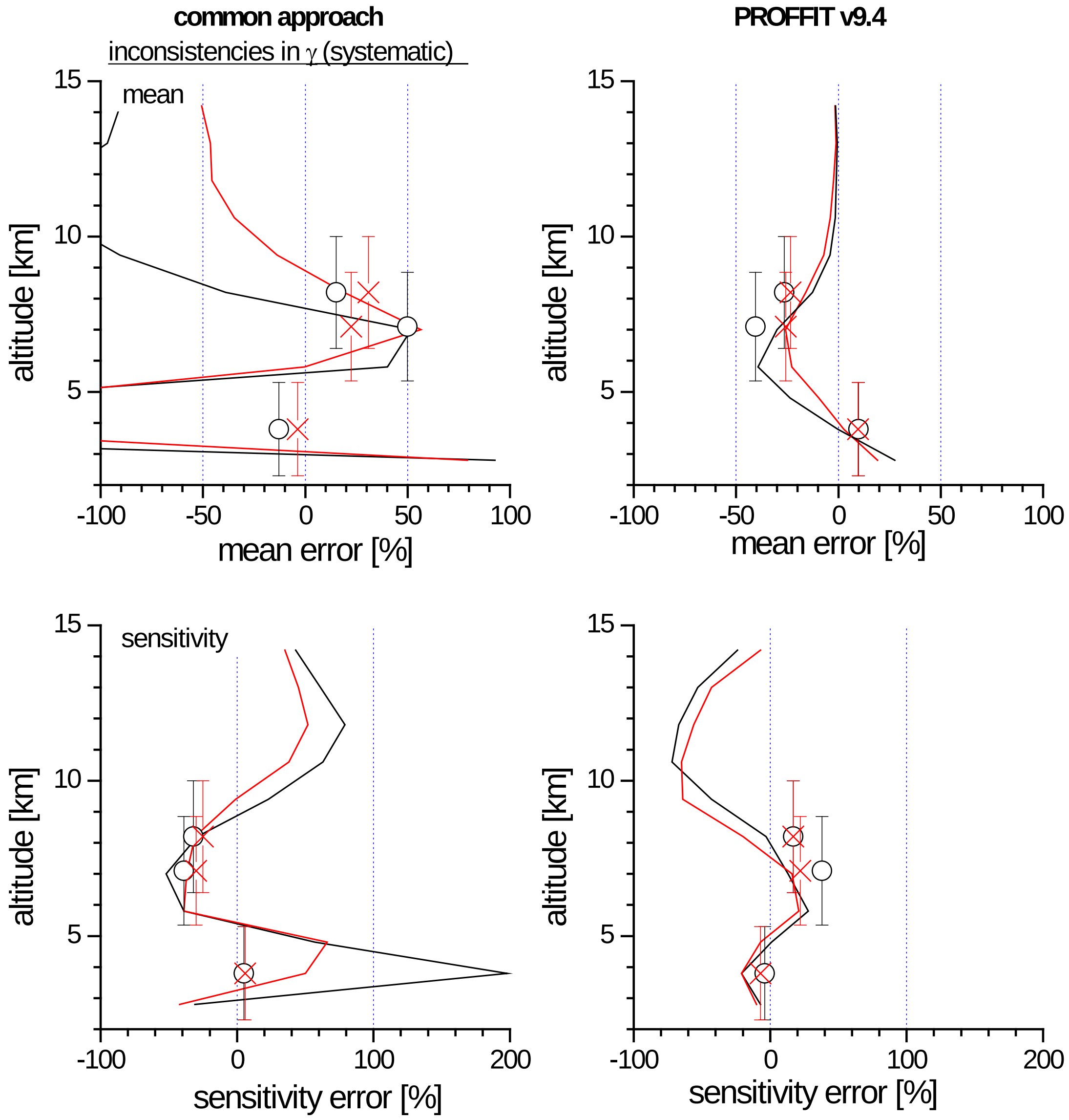


This systematic error source leads to random errors in δD due to non-linearities.

The error source is not common for HDO and H_2O → large error when common retrieval is applied

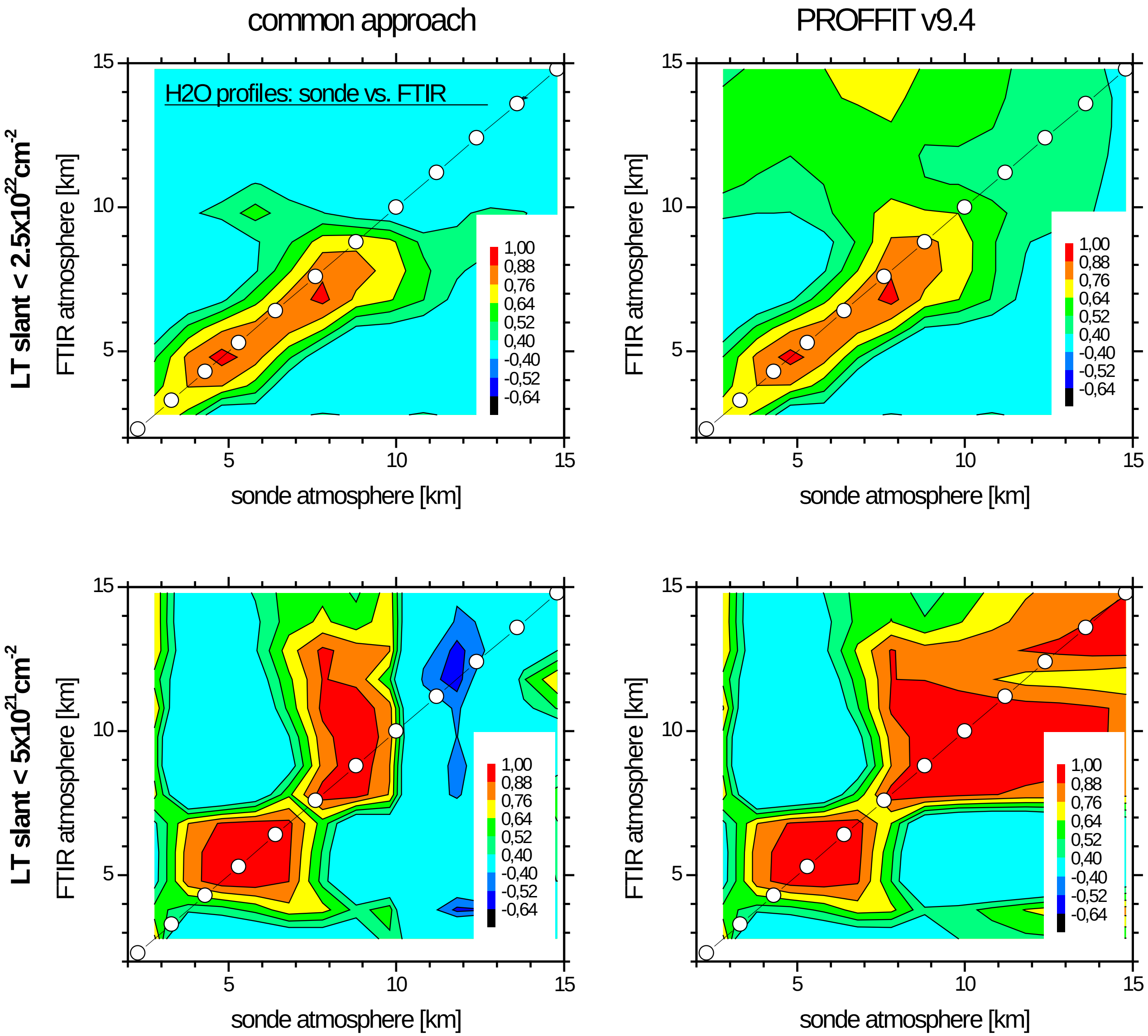
Inter-species constraint forces common response of HDO and H_2O → reduced error in ratio for unsaturated H_2O lines, but still large

Inconsistency in line shape of H_2O and HDO (γ(HDO) 2% increased)



Systematic errors are larger for common approach

Empirical validation of H_2O profiles: ptu-sonde vs. FTIR:

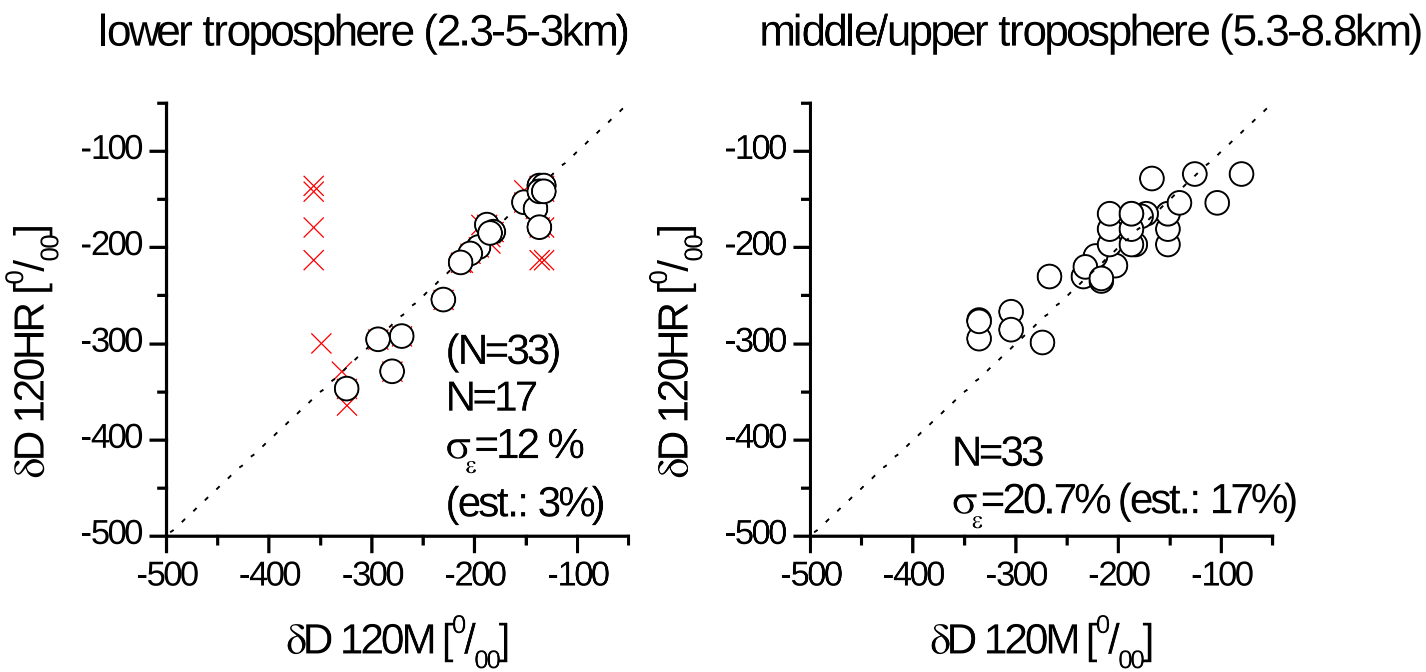


Inter-species constraint not only improves quality of δD profiles but also quality of H_2O profile:

H_2O retrieval benefits from additional information present in HDO lines

Detection of UT/LS H2O with the proposed lines ?
For a definitive conclusion we need a larger ensemble of compared profiles (the correlation shown here bases on only 7 profiles) !

120M ↔ 125HR intercomparison (January, March, and April 2005)



This intercomparison allows an empirical assessment of the error due to measurement noise !

It confirms that the boundary layer δD value varies strongly on small timescales.

Lower troposphere: for measurements within 1h 12% error → in slight disagreement with theoretical estimation of 3%.

Middle/upper troposphere: for measurements within 3h 21% error → in best agreement with theoretical estimation of 17%

Is there a correlation with hurricane activity ??