Response to Reviewer #2

We thank the reviewer for his comments and suggestions.

For example, heavy isotopes of hydrogen should be written as ^{2}H rather than as D according to IUPAC: Nomenclature of Inorganic Chemistry. IUPAC Recommendations 2005, RSC Publishing, Cambridge, UK, 2005. So in all instances where D has been used instead of ^{2}H, D must be replaced by ^{2}H.

This has been changed throughout the manuscript. However, we want to point out that the mentioned IUPAC recommendations state that "hydrogen is an exception to the rule in Section IR-3.3.1 in that the three isotopes …. can have the alternative names protium, deuterium and tritium, respectively. The symbols D and T may be used for deuterium and tritium …"!

Similarly, in equation (1) the factor 1000 has to be removed to meet the latest IUPAC guidelines

Has been changed. But again we want to point out that Coplen (2011, Table 2 and Table 3) state explicitly that isotope ratios should be given in per mil. Even if we remove the factor of 1000 in the equation (which we did now) we finally have to multiply the values by 1000 to give the values as recommended by Coplen (2011)!

and recommended terms of stable isotope ratio measurements and reporting results thereof (Coplen, T.B., 2011, Rapid Commun. Mass Spectrom., 25, 253 the authors should note a H2 cylinder gas cannot and must not be used as a 'reference gas' but at best as a monitoring gas. Since the H2 cylinder gas is neither introduced into the IRMS directly

The reference gas is injected directly into the IRMS. This has been clearly described in the section "Isotope Ratio Mass Spectrometer".

nor meets the conditions of a reference material distributed by either the IAEA or NIST it does not meet the requirements of a 'reference gas', It's sole purpose is that of a monitoring gas. For this reason sample δ2H values thus measured and calculated may not be reported v. VSMOW since they were not properly scale normalized on the VSMOW/SLAP scale on the basis of 2 contemporaneously analyzed reference materials. Pulses of H2 'reference gas' from a gas cylinder cannot be used for calibration of δ2H values, because such practice would violate the principle of identical treatment of sample and standard where all analyte gases must pass though the same preparative-analytical sequence.
'Reference gas' pulses from an H2 cylinder are not generated in the same fashion as H2 analyte gas from organic matter, do not pass through a GC prior to isotopic measurement, and thus are not subject to the same potential fractionations. The availability of a wide range of hydrogen stable isotope RMs for online analytical applications eliminates the justification of using outdated and indefensible 1-point

calibration and the employment of H2 ‘reference gas’ pulses except for monitoring IRMS performance and generation of raw δ 2H values. Due to the wide range of the VSMOW/SLAP scale, for hydrogen isotopes only 2-point calibration can adequately account for the scale compression of individual isotope ratio mass-spectrometer systems. Therefore, 2-point calibration vs. calibrated Reference Materials is strongly recommended in order to achieve best accuracy and international comparability in hydrogen isotope analysis. In the light of the fact that determination of reported δ2H values does not meet the aforementioned IUPAC guidelines and recommended terms of stable isotope ratio measurements and reporting results thereof, this manuscript can only be accepted (after major revision) as a proof-of-concept paper reporting non scale normalized δ2H values. Presenting their δ2H values determined as described as δ2H v. VSMOW values is incorrect and, in fact misleading.

We used two different gases to calibrate our measurements. One hydrogen reference gas calibrated against V-SMOW and a mixture of VOC of known isotope ratios. We changed the notation of the VOC mixture to “test mixture” and avoided the notation as a “standard”. The reviewer is right that this is not a standard in the meaning of the word. The hydrogen reference gas is calibrated against V-SMOW. The isotope ratio has been given in the text. However, we want to point out that the reference gas (hydrogen) cannot be passed through the whole system. That is the reason why we used a test mixture of the VOC of interest, the isotope ratios of which have been determined by an independent laboratory. They calibrated these measurements against IAEA-SMOW, IAEA-GISP, and IAEA-SLAP. This test mixture is indeed measured using exactly the same procedure as for the air sample measurements, i.e. sample preconcentration, chromatographic separation, pyrolysis and injection into the IRMS. This is a standard procedure for continuous flow - isotope ratio mass spectrometry.

On the subject of reporting δ2H values properly scale normalized to VSMOW using 2 reference materials as scale anchors, more information is required detailing as to how independent 2H analysis was carried out by Agroisolab.

Additional information has been added to the text.

For starters clarification is required if indeed as stated on page purce compounds were analysed for 2H abundance by elemental analysis (EA). Typically, 2H analysis of organic compounds requires high temperature conversion elemental analysis (TC/EA). On page 11 the authors state "at 1723 K the methane signal was below the lower limit of detection. This is in stark contrast to what is shown in Figure 7. In Fig. 7 at 1723 K a blue band/box is shown for the relative peak areas of a CH4 signal while on the other hand there is no grey band/box thus indicating there was no detectable H2 peak. Similarly, on the same page the authors state "below 1173 K no H2 is produced and this no H2 signal is detectable. Again this does not match what is shown in Figure 7. At 1173 K this figure shows a grey band representing the relative peak area range of detected H2 signals.

This statement refers to Figure 7 in the first version of the manuscript, which was not published but subject to a quick review. Prior to the submission of the discussion paper

we noticed an incorrect reference to the colours in the figure and changed it accordingly, which changed to Figure 6 due to merging of two Figures as recommended by one of the reviewers. When the reviewer would have read the published version he could have avoided this misunderstanding!

Further down on page 7 the authors state "the same measurement series was analysed 'using' H3+ factors of 5.0, 5.3 and 5.8". Were these H3+ factors set arbitrarily, i.e. irrespective of what actual H3+ factor was determined by the system? If so, this test makes no sense whatsoever. Correcting measurements for an H3+ factor of e.g. 5.8 if the system test determined the current H3+ factor to be e.g. 4.8 will of course affect results. One can only hope the way this sentence is phrased does not accurately reflect what actually happened.

The reviewer is right that using a different H3+ correction as determined by the system would lead to different results and does not make any sense. However, as described in the text a repeated determination of this factor led to larger variations as expected. Therefore, we reanalyzed the measurements using the H3+ factors given in the text in order to get an idea of the uncertainties due to the impact of this factor.