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RESEARCH ARTICLE

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Organic contamination detection for isotopic analysis of water by laser spectroscopy

Cody Millar[1] | Kim Janzen[1] | Magali F. Nehemy[1] | Geoff Koehler[2] | Pedro Hervé-Fernández[1,3,4] | Jeffrey J. McDonnell[1,5]

[1]Global Institute for Water Security, School of Environment and Sustainability, University of Saskatchewan, 11 Innovation Boulevard, Saskatoon, SK, S7N 3H5, Canada

[2]NHRC Stable Isotope Laboratory, Environment and Climate Change Canada, 11 Innovation Boulevard, Saskatoon, SK, S7N 3H5, Canada

[3]Instituto de la Patagonia, Departamento de Hidrobiología, Universidad de Magallanes, Punta Arenas, Chile

[4]Facultad de Ciencias Liberales, Universidad Adolfo Ibañez, Viña del Mar, Chile

[5]School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham, UK

Correspondence
C. Millar, Global Institute for Water Security, School of Environment and Sustainability, University of Saskatchewan, 11 Innovation Boulevard, Saskatoon, SK, S7N 3H5, Canada.
Email: cody.millar@gmail.com

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Rationale: Hydrogen and oxygen stable isotope ratios (δ^2H, $\delta^{17}O$, and $\delta^{18}O$ values) are commonly used tracers of water. These ratios can be measured by isotope ratio infrared spectroscopy (IRIS). However, IRIS approaches are prone to errors induced by organic compounds present in plant, soil, and natural water samples. A novel approach using ^{17}O-excess values has shown promise for flagging spectrally contaminated plant samples during IRIS analysis. A systematic assessment of this flagging system is needed to prove it useful.

Methods: Errors induced by methanol and ethanol water mixtures on measured IRIS and isotope ratio mass spectrometry (IRMS) results were evaluated. For IRIS analyses both liquid- and vapour-mode (via direct vapour equilibration) methods are used. The δ^2H, $\delta^{17}O$, and $\delta^{18}O$ values were measured and compared with known reference values to determine the errors induced by methanol and ethanol contamination. In addition, the ^{17}O-excess contamination detection approach was tested. This is a post-processing detection tool for both liquid and vapour IRIS triple-isotope analyses, utilizing calculated ^{17}O-excess values to flag contaminated samples.

Results: Organic contamination induced significant errors in IRIS results, not seen in IRMS results. Methanol caused larger errors than ethanol. Results from vapour-IRIS analyses had larger errors than those from liquid-IRIS analyses. The ^{17}O-excess approach identified methanol driven error in liquid- and vapour-mode IRIS samples at levels where isotope results became unacceptably erroneous. For ethanol contaminated samples, a mix of erroneous and correct flagging occurred with the ^{17}O-excess method. Our results indicate that methanol is the more problematic contaminant for data corruption. The ^{17}O-excess method was therefore useful for data quality control.

Conclusions: Organic contamination caused significant errors in IRIS stable isotope results. These errors were larger during vapour analyses than during liquid IRIS analyses, and larger for methanol than ethanol contamination. The ^{17}O-excess method is highly sensitive for detecting narrowband (methanol) contamination error in vapour and liquid analysis modes in IRIS.

1 | INTRODUCTION

The stable isotopes of hydrogen and oxygen are used widely to investigate water cycling through the hydrosphere.[1,2] For analyses of rainfall, streamflow, and groundwater, isotope ratio infrared spectroscopy (IRIS) has revolutionized the field with its low cost and high frequency potential.[3–6] IRIS systems have many advantages. They are as accurate as traditional isotope ratio mass spectrometry (IRMS) approaches for pure water,[7] allow researchers to bypass previous analysis bottlenecks, and are now available as portable units allowing for real-time analyses and flexible sampling decision making.[8] This has resulted in the proliferation of soil–plant–atmosphere isotope data using such IRIS methods as the Los Gatos Research (LGR; Los Gatos Research Inc., San Jose, CA, USA) off-axis integrated cavity output spectroscopy (OA-ICOS) system and the Picarro (Picarro, Santa Clara, CA, USA) cavity ring down spectroscopy (CRDS) system.

But, as ecohydrologists begin to address plant water use patterns from variable subsurface sources,[1,5,8–10] users of IRIS systems face a major methodological challenge. That is, analytes extracted from plants and soils for stable isotope analyses of hydrogen and oxygen can contain co-extracted soluble organic compounds in addition to the extracted water.[11,12] These organic compounds are known to introduce substantial errors in isotopic measurements when analysed via IRIS methods,[7,11,13–15] especially during vapour-mode analyses.[16] Thus, these potentially contaminated samples are typically measured by IRMS, which is not prone to error when analysing samples with trace amounts of organic compounds.[11,13,14]

Brand et al[13] studied the effect of methanol (CH_3OH; MeOH) and ethanol (C_2H_6O; EtOH) contamination in prepared water samples analysed using a Picarro CRDS system by comparing these results with those produced by thermal conversion/elemental analyser IRMS. During the CRDS analysis, they showed that methanol contamination caused more significant errors than ethanol contamination. Furthermore, they found that both methanol and ethanol contamination caused IRIS results to differ from IRMS results. West et al[11] advanced this research by analysing water extracted from eleven plant species and one organic soil using IRIS and IRMS methods. They found that organic contaminants in the analytes, for over half the samples, caused significant and substantial deviations between the two methods. Interestingly, they also showed that CRDS and OA-ICOS systems produced different results (negative versus positive error directions for each analysis approach) when exposed to the more strongly contaminated plant analytes.

The source of these errors in IRIS analyses, known as spectral interference, relates to the measurement method.[13] IRIS systems utilize highly specific photoabsorption characteristics, relatively unique to water isotopologues ($^1H^1H^{16}O$, $^1H^2H^{16}O$, $^1H^1H^{17}O$, and $^1H^1H^{18}O$). These characteristics are used to determine the isotope ratios (δ^2H, $\delta^{17}O$, and $\delta^{18}O$ values) of the analyte.[13] Organic compounds in the analyte that share spectral absorption features with water, specifically the O-H bond, can result in interference-related measurement errors.[13] It is not the isotopic composition of the contaminants that causes the errors, but rather the absorption features of the O-H bond in the contaminants that cause spectral interference. The two most commonly cited organic compounds present in extracted plant analytes are methanol and ethanol[7,11,13,14,16–18] with secondary compounds such as glycols, phenols, carbohydrates, and some terpenes also having troublesome O-H bonds that could cause IRIS measurement errors.

Accurate determination of organic compound content in natural samples requires organic content analysis for each sample in a given sampling campaign. However, direct analysis of water samples for organic compound content is sample-, time-, and cost-intensive. Due to these issues, ecohydrological studies rarely carry out or include organic compound content analysis details for their sampled waters. However, our previous research noted that methanol and ethanol content for analytes extracted from wheat samples were between 0.007% and 0.24% (v/v) and 0.02% and 3.8% (v/v), respectively. This was dependent on the method of water extraction, and the portion of the wheat plant from which the water was extracted.[12] Given the unique organic compound content of different plant species[19–21] and intra-plant components,[12] and even as a result of seasonal changes in metabolic processes within the same species,[22–25] natural variations in organic compound content are notable.

So, what can be done about these contamination-driven errors? A simple solution would be to analyse all samples with contamination concerns using IRMS. However, this is not realistic. IRMS analysers cost substantially more than IRIS systems. Indeed, the lower cost of IRIS systems has allowed for the proliferation of H and O stable isotope data and democratization of access to this data. Various approaches for dealing with contaminated samples for IRIS systems exist, such as pre-processing of samples, and post-processing detection and correction.[7,11,14,16,26,27] Pre-processing approaches for IRIS systems include the use of tools such as activated charcoal[11] or micro-combustion modules.[14,26] Potentially contaminated water samples can have activated charcoal added to them or be pushed through activated charcoal filters wherein the organics should be adsorbed. This approach has shown limited success, with one study showing deviations as large as 35‰ for δ^2H values and 11.8‰ for $\delta^{18}O$ values after charcoal use.[11] The micro-combustion module for CRDS analysers heats sample to 200°C to remove combustible compounds from the analyte before analysis. This approach has successfully removed organic compounds and decreased spectral contamination-driven errors in isotope results,[14,26] but the use of a proprietary catalyst precludes this method for many users. LGR does not manufacture an inline combustion module for OA-ICOS devices, so this approach is limited to Picarro CRDS users.

For post-processing contaminant detection, one such tool is the LGR Liquid Water Isotope Analyzer–Spectral Contamination Identifier (LWIA-SCI) software. This software is used to detect spectral interference during liquid water analysis via OA-ICOS.[7,27] In cases where contaminants are detected, and the sources are known, protocols for correcting the isotope ratios of contaminated samples have been suggested. For OA-ICOS systems the protocols for

correction will be device specific.[7,27] CRDS analysers have access to the PostProcess ChemCorrect software by Picarro. This software does not correct the contaminated data, but rather shows the magnitude of the contamination and its potential sources.

Accurate correction requires knowing which contaminants are present and in what concentrations. The latter is not always possible due to budget, time, extraction, and analysis device specifics, and/or sample constraints. Although contaminant sources are not always known, post-processing corrections have been developed using methanol and ethanol and applied in ecohydrological research.[14,28] Approaches for the detection and correction of contamination are even more limited for vapour-mode analyses by OA-ICOS. With the recent increase in studies using the direct vapour equilibration (DVE) method for plant and soil isotope analysis,[29–33] a contaminant detection approach is sorely needed. A recent study[16] used calculated ^{17}O-excess values as a proxy contaminant detection tool during OA-ICOS vapour-mode analyses of woody plants. It showed that organic contamination could be a problem during the vapour-mode analysis of these types of samples, but that its detection is possible with the ^{17}O-excess approach.

Building on work[11,13,14] that has shown significant differences between IRMS and IRIS isotope results when analysing contaminated samples, we present an analysis of the effects of methanol and ethanol contamination on isotope results measured using the OA-ICOS device. We go beyond this previous research, by analysing methanol- and ethanol-contaminated samples with the newer DVE-OA-ICOS system (analysed via vapour-mode using the OA-ICOS device and hereafter referred to as vapour-mode) and comparing results with those from the standard liquid-mode using OA-ICOS (hereafter referred to as liquid-mode) for comparison with IRMS results. This study seeks to quantify and compare the effects of increasing methanol and ethanol concentrations on measured isotope results between liquid mode and vapour mode. Further, we test the recently developed ^{17}O-excess contamination detection approach for its effectiveness at identifying the presence of spectral interference during liquid-mode OA-ICOS analyses. A threshold range for acceptable ^{17}O-excess values is proposed in this work to improve its effectiveness as a proxy contamination flagging system.

Our three main questions are:

1. How do isotope results from liquid- and vapour-mode OA-ICOS analyses compare with liquid IRMS results for samples at the same contaminant concentrations?
2. Does organic contamination-induced spectral interference generate the same errors during liquid- and vapour-mode OA-ICOS analyses?
3. Can isotope results corrupted by contamination be detected using the ^{17}O-excess approach after liquid- and vapour-mode OA-ICOS analyses?

Our goal is to provide OA-ICOS users with a tool for contaminant detection in liquid-mode and especially vapour-mode without the need for additional equipment beyond the analyser.

2 | MATERIALS AND METHODS

2.1 | Contaminated and control samples

A set of contaminated water samples was prepared using tap water, and dilutions of methanol (Fisher Chemical, Hampton, NH, USA; 99.9% by volume) and ethanol (Commercial Alcohols, Greenfield Global Inc., Toronto, ON, Canada; 100% by volume). The isotope ratios for the tap water as analysed by liquid mode were: δ^2H, −132.50 ± 0.45‰; δ^{17}O, −8.81 ± 0.10‰; δ^{18}O, −16.24 ± 0.09‰ ($n = 10$). This set of uncontaminated samples measured by liquid-mode OA-ICOS ($n = 10$) was used as our reference water (ROw) for all statistical analyses and error comparisons. Controls for IRMS ($n = 10$) and vapour-mode ($n = 4$) analyses were prepared with samples of the tap water. The δ^2H values of the methanol and ethanol used in this study were measured via IRMS, although it was not possible to measure the δ^{18}O values of the contaminants with our system. The methanol had a δ^2H value of −163.02‰ ($n = 5$; SD: 0.47‰). The ethanol had a δ^2H value of −179.53‰ ($n = 5$; SD: 0.52‰). Thirteen bottles of methanol–water mixtures and ten bottles of ethanol–water mixtures were prepared. From these bottles five subsamples were generated ($n = 5$) per contaminant concentration per method of analysis (liquid-mode, vapour-mode, IRMS). For all methanol–water and ethanol–water mixtures we designate the organic compound and its concentration in this way: contaminant-concentration. Thus, for a methanol–water mixture with 0.001% (v/v) concentration, the designation would be MeOH-0.001%. MeOH–water mixtures were prepared at 0.001%, 0.002%, 0.004%, 0.008%, 0.01%, 0.016%, 0.032%, 0.064%, 0.1%, 0.128%, 0.256%, 0.5%, and 1.0% (v/v) concentrations. EtOH–water mixtures were prepared at 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, 0.25%, 0.5%, 1.0%, 5.0%, and 10.0% (v/v) concentrations. Different concentrations were used for methanol and ethanol due to pilot study findings indicating that OA-ICOS had higher sensitivity to methanol contamination.

The vapour-mode dataset utilized in this study was also used in Nehemy et al[16] who compared results from field-collected plant and soil samples with the vapour-mode data we generate here using laboratory-prepared methanol- and ethanol-contaminated samples. We expand that work by adding ^{17}O-excess detection of liquid-mode samples for comparison with the DVE dataset, and by defining a range of acceptable ^{17}O-excess values for use as a flagging system.

2.2 | Isotope analyses

δ^2H, δ^{17}O, and δ^{18}O values are expressed in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW).[34,35] We use two internal laboratory standards for calibration: CSNOW: −202.6‰ (δ^2H), 14.08‰ (δ^{17}O), and −26.51‰ (δ^{18}O); LVIC: 9.7‰ (δ^2H), −0.1‰ (δ^{17}O), and 0.57‰ (δ^{18}O). Our internal laboratory standards are calibrated using the international standards VSMOW2 and VSLAP2. Calibration of water standards for δ^{17}O values follows a previously reported normalization approach.[36]

The isotope composition of liquid- and vapour-mode samples was measured using an LGR TWIA-45EP OA-ICOS device, an Elementar Isoprime IRMS device (Elementar UK Ltd, Cheadle, UK), and a Delta V IRMS device (Thermo Fisher Scientific, Waltham, MA, USA). In liquid mode, the OA-ICOS analyser has a precision of ±1.0‰ (δ^2H), ±0.2‰ (δ^{17}O), and ±0.2‰ (δ^{18}O). In vapour mode, for a 30 s reading period, the OA-ICOS analyser has a precision of ±1.8‰ (δ^2H), ±0.25‰ (δ^{17}O), and ±0.3‰ (δ^{18}O). Typical IRMS precisions are ±1.5‰ (δ^2H) and ±0.14‰ (δ^{18}O). We note here that our precisions for OA-ICOS are calculated in-house and are not the same as those commonly cited from the manufacturer's manual.

For analyses using IRMS, hydrogen isotope compositions were determined by reduction of a 0.8 μL sample to hydrogen by reaction with elemental chromium in a quartz reactor at 1030°C.[37] The resultant H_2 gas was separated on a 5 Å molecular sieve gas chromatography column and introduced into the Elementar Isoprime IRMS device. Two replicates of each sample were injected and the first replicate for each sample was discarded to minimize memory effects. Resultant raw delta values of the measured hydrogen were normalized to the VSMOW–VSLAP scale by analyses of two calibrated reference waters: CSNOW and LVIC. For oxygen isotopes, the CO_2–H_2O equilibration technique was used.[38] A system comprising a GasBench II interface and a sample preparation device (both from Thermo Fisher Scientific) connected to a Delta V IRMS system was used at 25°C for all CO_2–H_2O equilibrations. Results are reported relative to the VSMOW–VSLAP scale by normalizing to the aforementioned CSNOW and LVIC standards. For this research, only δ^2H and δ^{18}O values are measured via IRMS.

For vapour-mode analyses (via DVE-OA-ICOS), previously established analysis protocols were followed.[30] (1) 5 mL of sample (control or contaminant–water mixture) was placed into a 17.8 cm × 20.3 cm Leakproof bag (Uline, Pleasant Prairie, WI, USA, no. S-5855) with a double-locking airtight zipper. (2) Before analysis, the bag headspace was filled with dry air and allowed to equilibrate with the samples for 24 h at room temperature (*ca* 22°C). Sample analysis also occurs at room temperature. (3) A headspace sampling apparatus was used to draw vapour from the sample bags into the OA-ICOS instrument. This apparatus was composed of a 21G stainless steel needle connected to a 1 m long by 0.95 mm impermeable Teflon line attached to the OA-ICOS analyser's vapour port. Before sampling, the needle was connected to a Drierite laboratory gas drying unit (W. A. Hammond Drierite Co. Ltd, Xenia, OH, USA) until the internal water content of the OA-ICOS analyser was below 500 ppmv H_2O. (4) The headspace of controls, contaminant–ROw, and water standards bags were sampled, on average for two minutes, by piercing the sample bag with the needle. (5) δ^2H, δ^{17}O, and δ^{18}O values were noted when the measured headspace vapour content stabilized at *ca* 28 000 ppmv H_2O for at least one minute and the standard deviations (SDs; i.e. ±1 SD) of the raw isotope data were less than ±1.0‰ for all measured isotopes; ±1 SD corresponds to a reading period of 1 min. (6) The sampling needle was reconnected to the Drierite unit between all measurements, as noted in step (3). (7) In-house water standards were alternated and analysed with contaminated samples every four samples (bracketed normalization method) and a control tap water sample was run every eight samples. For example, a given analysis sequence would follow this pattern (listing the order of samples analysed): Standard 1, sample(s) 1, s2, s3, s4, Standard 2, s5, s6, s7, control, Standard 1. At this point the pattern would be repeated with new samples (s8 onward in this case) being added to the 'sample' slots as the analyses progressed. After sampling from the standard bags, the bags were re-sealed with tape. Two water standards (CSNOW, LVIC) were used to normalize the data using the bracketed normalization method, which minimized and controlled analysis drift. 10 mL of each standard was used during isotopic analyses.

We clarify here that during OA-ICOS analyses for both liquid and vapour modes, the OA-ICOS measurement cavity analyses a vapour. During vapour-mode analysis, the OA-ICOS device draws into its measurement cavity a vapour from the analysis bag which is in isotopic equilibrium with the liquid sample. During liquid-mode analysis, the OA-ICOS device first draws liquid from the sample vial, and the liquid is then completely vaporized in the heated injector before expansion into the measurement cavity.

2.3 | Contamination detection

Two contamination detection approaches are used in this study: the LGR LWIA-SCI software and the newly developed ^{17}O-excess approach.[16] The software was developed to detect spectral contamination during liquid water analysis.[7,27] This software was used during post-processing of the liquid-mode isotope data to flag which contaminant–water mixtures had narrow and broadband spectral contamination, as defined by the LGR software. The LWIA-SCI software was set at a detection limit of ±3 SD for both spectral bands during contaminant detection of liquid-mode samples. The results of flagging with the software are compared with the results of ^{17}O-excess flagging as a means of testing the efficacy of the ^{17}O-excess approach in identifying contaminated samples in liquid-mode analyses. Previously, the ^{17}O-excess approach effectively detected even low levels of contamination after vapour-mode analyses of plant samples and laboratory-prepared samples of known contaminant concentrations.[16] We improve on that work by developing a more robust approach to this flagging system.

As with deuterium excess[39] (d-excess), divergence from the established relationships between $\delta^{17}O/\delta^{16}O$ and $\delta^{18}O/\delta^{16}O$ ratios is defined as[40,41]

$$^{17}\mathrm{O}-\mathrm{excess}=\delta'^{17}\mathrm{O}-0.528\delta'^{18}\mathrm{O} \quad (1)$$

where $\delta'^{17}O = \ln(\delta^{17}O + 1)$, $\delta'^{18}O = \ln(\delta^{18}O + 1)$, and 0.528 is the slope of the global meteoric water line. As ^{17}O-excess values are very close to zero, they are typically multiplied by 10^6 and are reported in per meg.[41] IRIS instruments cannot achieve the per meg precisions necessary for routine δ^{17}O measurements of natural waters without repeated sample measurements, statistical analysis, and relatively long

integration periods.[42,43] However, for use as an organic contamination detection tool, the precisions required can be considerably less. As such, ^{17}O-excess measurements are reported in per mil (‰) for this study. The δ^{17}O precision for our OA-ICOS devices is ±0.2‰ (200 per meg).

Globally, natural variation in ^{17}O-excess values of surface and meteoric waters tends to be small and in the approximate range −45 to 54 per meg (−0.045‰ to 0.054‰) (surface waters) and −250 to greater than 100 per meg (−0.25‰ to 0.1‰) (meteoric waters).[44] The tap water used in this study has a ^{17}O-excess range between −0.32‰ and −0.08 ± 0.2‰, which overlaps with the range of natural variation.[44]

A useful contamination detection tool aims to indicate when a sample is contaminated *and* when the isotope data deviate by a significant amount from an acceptable range. A contamination detection approach that flags samples whose results are erroneous is helpful, but a detection approach that flags unproblematic data is not. Previously, soil water ^{17}O-excess values were used to validate a range of acceptable ^{17}O-excess values for plant water (not contaminated by organics) and assumed to reflect the site's natural ranges of isotopic composition.[16] That work found that those values were often close to zero. We go beyond that work by defining a range of ^{17}O-excess values that are acceptable (no problematic contamination) and are unacceptable (problematic contamination). Since natural waters can have non-zero ^{17}O-excess values,[41,44] a 'close-to-zero' metric is not precise enough when used as the metric for indicating contamination.

To define ^{17}O-excess contamination detection thresholds, δ^{17}O and δ^{18}O values were measured during vapour- and liquid-mode OA-ICOS analyses of the reference water and contaminant–water mixtures. ^{17}O-excess values were then calculated using Equation 1. In addition, *Z*-scores were calculated from the isotope data for each of the contaminated samples; *Z*-scores are used to note when those isotope data became unacceptably different from the reference water isotope ratios. The *Z*-scores are then used to inform the range of acceptable and unacceptable ^{17}O-excess threshold values, and are calculated following a previous approach[45]:

$$Z = \frac{E - W}{\mu} \quad (2)$$

where E is the δ^2H or δ^{18}O value of the contaminated samples, W is the δ^2H or δ^{18}O value of the reference water, and μ is the target SD of 2.0‰ (δ^2H) and 0.2‰ (δ^{18}O). In this study a *Z*-score of less than |3| is considered acceptable, |3–6| is questionable, and greater than |6| is unacceptable. While we adopted the previously established target SD,[45] other studies[14] have suggested larger target SD ranges for accuracy analysis in hydrological research. We use the previously established target SD in order to develop a more strict ^{17}O-excess detection threshold. However, we chose a slightly larger range for acceptable, questionable, and unacceptable (relative to the original approach[45]) given the comparison of different analysis approaches.[46]

Previous research showed that methanol caused larger deviations in isotope results than ethanol.[11,14] Thus, we derive our ^{17}O-excess threshold from methanol results only. The *Z*-scores showed that for liquid-mode samples at MeOH-0.008% and higher, the isotope results become unacceptable and differed widely from those of the reference water (Figure 2, Table 2). The ^{17}O-excess for liquid-mode MeOH-0.008% is 0.38‰ (SD: ±0.05‰). As such we define a ^{17}O-excess threshold based on the MeOH-0.008% ^{17}O-excess score, accounting for the SD. Thus, for all vapour- and liquid-mode OA-ICOS results:

- ^{17}O-excess value < |0.43‰| is acceptable, indicating no problematic contamination.
- ^{17}O-excess value ≥ |0.43‰| is unacceptable, indicating problematic contamination.

Isotope data were plotted in [δ^{18}O, δ^{17}O] as a visual indicator of contamination. A ^{17}O-excess value of zero would be expected to fall on the ^{17}O global meteoric water line. Given the above defined threshold, ^{17}O-excess data falling above or below the|0.43‰| band of the ^{17}O global meteoric water line slope (≥|0.43‰| for δ^{17}O, and >|0.75‰| for δ^{18}O) are problematically contaminated (see green shaded area in Figure 5).

2.4 | Statistical analyses

Means and SDs (±1 SD) were calculated for the reference, control, and contaminated samples for all isotope analyses to quantify data consistency. The δ^2H, δ^{17}O, and δ^{18}O values for the reference water analysed by liquid mode ($n = 10$) were considered the reference values for all statistical analyses. The δ^2H, δ^{17}O, and δ^{18}O relative error (trueness) (in ‰) was calculated for all samples and all analysis types. The relative error is the difference between the measured δ^2H, δ^{17}O, or δ^{18}O value (‰) of a given sample, and the respective δ^2H, δ^{17}O, or δ^{18}O value (‰) of the reference water analysed by liquid-mode OA-ICOS.

Because methanol and ethanol are more volatile than water, Raoult's law was utilized to determine the vapour-phase concentrations of methanol and ethanol in the analysis headspace of vapour-mode samples. We carried out this calculation as the DVE method samples the vapour-phase headspace and not the original liquid in the sampling bag. DVE methods operate on the principle that the water constrained in a plant, soil, or pure water sample will be in isotopic equilibrium with vapour in the headspace above that sample. Thus, it is possible to measure the hydrogen and oxygen isotope ratios of a given sample. However, when samples contain organic compounds, the measured headspace can see increased concentrations of those contaminants if they have a higher vapour pressure than water. The vapour-phase concentrations of contaminants in vapour-mode samples are utilized to explain the difference in results observed between vapour- and liquid-mode OA-ICOS results.

The contaminated sample isotopic results were compared using a one-way ANOVA for *a priori* comparisons. A Dunnet *a posteriori* test was selected for groups compared with the reference water. Although not all sample groups were normally distributed, all of them showed a

homoscedastic distribution within groups. ANOVA is a robust statistical test to use when violating the assumption of normality. Hence, the previously mentioned statistical tests were used. The statistical significance level was set to 0.05 ($\alpha = 0.05$).

3 | RESULTS

3.1 | Effects of contamination on isotope analyses

Table 1 summarizes the isotope ratio descriptive statistics for the reference, control, and contaminated samples analysed via liquid-mode, vapour-mode, and IRMS. Vapour-mode results exclude data from methanol samples >0.016% and ethanol samples >0.25%, as these samples showed apparent negative absorbance on the absorption plot during analyses. The latter is probably an artefact induced by contaminant-driven spectral interference and results in non-real starting conditions for the OA-ICOS device's mathematical models, which are used to build these data points. These excluded data do not appear in figures, tables, or any subsequent analyses.

During OA-ICOS analysis, methanol contamination had a more substantial effect on measured isotope ratios than ethanol contamination (Table 2). This was the case for both vapour- and liquid-mode analyses. Regarding error relative to the reference water, methanol contamination caused vapour- and liquid-mode OA-ICOS results to skew in a positive direction for δ^2H, δ^{17}O, and δ^{18}O values. However, ethanol contamination caused a mix of positive and negative relative errors for δ^2H, δ^{17}O, and δ^{18}O values. Neither methanol nor ethanol contamination caused significant errors in the IRMS isotope results.

Figure 1 shows all measured isotope ratios in dual-isotope space. IRMS data are not plotted in Figure 1 for clarity as those results fall within the following ranges relative to the reference water. For methanol-contaminated samples the IRMS results are within ±2.55‰ (δ^2H) and ±0.3‰ (δ^{18}O) of those of the reference water. For ethanol-contaminated samples the IRMS results are within ±1.89‰ and ±0.45‰ for δ^2H and δ^{18}O, respectively. Results produced by vapour mode and liquid mode show a strong linear relationship between increasing methanol concentration and measured isotope ratios: $R^2 = 0.994$ and 0.999 for vapour- and liquid-mode results, respectively (Figures 1A and 1B). However, increasing ethanol contamination did not result in a linear relationship between increasing contaminant concentration and measured isotope ratios: $R^2 = 0.338$ for vapour mode and $R^2 = 0.192$ for liquid mode (Figures 1C and 1D).

3.1.1 | Methanol-induced error

Figure 2 shows the *Z*-scores for vapour- and liquid-mode analyses for both contaminants. Methanol contamination had a far more significant effect on the stable isotope results for vapour- and liquid-mode OA-ICOS analyses than ethanol contamination.

For liquid-mode results, the measured δ^2H and δ^{18}O values became progressively more positive and the measurement errors became progressively larger as the methanol concentration increased. The error relative to the uncontaminated reference water is presented in Table 2. In terms of *Z*-scores, liquid-mode results were unacceptable at MeOH-0.008% and higher concentrations (Figure 2A).

The isotope ratios measured by vapour-mode followed a similar trend to that seen in liquid-mode OA-ICOS analyses. Notably, delta values and errors became progressively more positive and progressively larger with increasing methanol concentration. These errors were far larger than were seen in liquid-mode analyses (Table 2). The maximum relative error for vapour-mode results occurred at MeOH-0.016%, as concentrations above this value resulted in negative absorbance. Thus, the maximum relative mean error was 38.96‰ ($n = 5$) for δ^2H values and 21.82‰ ($n = 5$) for δ^{18}O values (see Table 2). For comparison, at this same methanol concentration, the error for liquid mode was 3.94‰ and 2.55‰ for δ^2H and δ^{18}O values, respectively. For *Z*-scores, nearly all the vapour-mode data fall into the unacceptable range for methanol-contaminated samples. MeOH-0.001% and MeOH-0.002% have one data point each where the δ^2H *Z*-scores fall into the acceptable range, while MeOH-0.001%, MeOH-0.002%, and MeOH-0.004% have eleven data points where the δ^2H *Z*-scores fall into the questionable range. However, for the aforementioned acceptable and questionable δ^2H *Z*-scores, their associated δ^{18}O *Z*-scores fall well into the unacceptable range.

For IRMS, the δ^2H and δ^{18}O errors were small and variable, with no progressive pattern as methanol contamination levels increased. As such, IRMS errors are not included in Table 2. The maximum δ^2H error (−2.55‰) occurred at MeOH-1.0% and the maximum δ^{18}O error (−0.31‰) at MeOH-0.1%. These errors barely fall outside the IRMS precision ranges (±1.5‰ for δ^2H and ±0.14‰ for δ^{18}O). All IRMS δ^2H and δ^{18}O results fall within the acceptable range for *Z*-scores, except for a single MeOH-0.1% δ^2H *Z*-score, which fell into the questionable range. As such, the IRMS results are not plotted in Figure 2 for clarity.

3.1.2 | Ethanol-induced error

For vapour- and liquid-mode analyses, ethanol contamination had relatively limited and inconsistent effects on measured stable isotope results and subsequent relative errors (Figures 1C and 1D; Tables 1 and 2). The δ^{18}O errors for liquid-mode analyses were skewed only in a negative direction and were not linear with increasing ethanol concentration. For liquid-mode δ^2H errors, there was a mix of positive and negative error directions, and these were not linear with increasing ethanol concentrations. In terms of *Z*-scores, the ethanol liquid-mode results fell within the acceptable range for ethanol concentrations of up to 0.25%. The EtOH-0.5% and EtOH-1.0% *Z*-scores fell into the questionable range, while the EtOH-5.0% and EtOH-10% liquid-mode *Z*-scores fell into the unacceptable range (Figure 2B).

Ethanol contamination also had a nonlinear effect on vapour-mode results. As for methanol, ethanol-induced errors were more

TABLE 1 Means and SDs of δ^2H, $\delta^{18}O$, $\delta^{17}O$, and ^{17}O-excess values from reference (ROw), control and methanol- and ethanol-contaminated samples. The stable isotope ratios for the reference water samples analysed by liquid-mode OA-ICOS are considered the reference (true) values ($n = 10$). Means of contaminated samples are from $n = 5$ data points. No data show for vapour-mode methanol concentrations higher than 0.016% and ethanol concentrations higher than 0.25% due to the negative absorbance issue

Reference and control ROw samples								
		δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)	
Sample ID	**n**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Liquid-OA-ICOS ROw	10	−132.50	0.45	−16.24	0.09	−8.81	0.10
Vapour-OA-ICOS control	4	−129.88	1.40	−16.01	0.24	−7.50	0.08
IRMS control	10	−131.99	1.27	−16.45	0.03	—	—

MeOH-contaminated samples																			
	Liquid-mode OA-ICOS results								**Vapour-mode OA-ICOS results**								**IRMS results**			
	δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)	
Sample ID	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
MeOH-0.001%	−131.70	0.39	−16.19	0.04	−8.62	0.07	−0.04	0.06	−123.56	1.75	−14.02	0.64	−6.53	0.29	0.90	0.30	−131.56	0.90	−16.21	0.02
MeOH-0.002%	−131.60	0.41	−15.97	0.07	−8.47	0.02	−0.01	0.02	−125.28	1.10	−13.67	0.17	−4.91	0.06	2.35	0.08	−130.42	0.92	−16.23	0.01
MeOH-0.004%	−131.35	0.44	−15.73	0.07	−8.33	0.19	0.00	0.22	−122.63	2.74	−11.57	0.27	−1.53	0.43	4.62	0.43	−130.66	0.75	−16.26	0.02
MeOH-0.008%	−130.16	0.12	−14.95	0.06	−7.55	0.08	0.38	0.05	−113.44	1.62	−6.45	0.33	6.87	0.29	10.27	0.40	−130.64	0.74	−16.26	0.02
MeOH-0.01%	−131.45	0.12	−14.88	0.09	−6.57	0.12	1.33	0.10	−94.47	8.27	1.46	0.68	17.12	2.47	16.20	2.58	−132.97	1.10	−16.30	0.33
MeOH-0.016%	−128.56	0.07	−13.69	0.07	−6.05	0.05	1.21	0.02	−93.54	1.44	5.58	0.33	40.11	1.96	36.39	1.97	−131.59	0.53	−16.51	0.03
MeOH-0.032%	−124.05	0.71	−10.39	0.07	−2.57	0.16	2.94	0.14									−131.54	0.77	−16.45	0.02
MeOH-0.064%	−115.37	0.26	−3.60	0.19	4.28	0.09	6.18	0.06									−131.47	0.68	−16.50	0.01
MeOH-0.1%	−103.51	0.17	3.07	0.10	14.45	0.04	12.73	0.07									−133.33	3.03	−16.55	0.02
MeOH-0.128%	−94.33	0.74	8.66	0.44	21.74	0.50	16.95	0.33									−132.20	0.85	−16.50	0.03
MeOH-0.256%	−51.17	0.26	35.60	0.06	52.60	0.16	32.79	0.13									−131.51	0.90	−16.50	0.03
MeOH-0.5%	25.08	0.34	81.25	0.28	101.00	1.64	54.97	1.42									−131.23	0.44	−16.47	0.02

(Continues)

TABLE 1 (Continued)

MeOH-contaminated samples																		
	Liquid-mode OA-ICOS results								Vapour-mode OA-ICOS results								IRMS results			
	δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)	
Sample ID	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
MeOH-1.0%	235.40	1.54	200.58	1.00	228.18	5.47	109.00	4.03									−135.05	1.77	−16.43	0.01
EtOH-contaminated samples																		
	Liquid-mode OA-ICOS results								Vapour-mode OA-ICOS results								IRMS results			
	δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)		^{17}O-excess (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)	
Sample ID	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
EtOH-0.001%	−133.60	0.39	−16.51	0.06	−8.89	0.09	−0.14	0.12	−124.07	3.26	−15.37	0.64	−9.20	1.14	−1.07	1.06	−132.61	0.54	−16.58	0.02
EtOH-0.005%	−133.40	0.13	−16.60	0.07	−8.86	0.10	−0.06	0.07	−128.41	1.30	−16.12	0.16	−8.91	0.12	−0.37	0.06	−132.35	0.70	−16.61	0.00
EtOH-0.01%	−133.30	0.10	−16.43	0.07	−8.75	0.09	−0.04	0.09	−123.02	6.71	−14.65	0.94	−7.58	0.40	0.18	0.33	−132.42	1.08	−16.61	0.03
EtOH-0.05%	−134.77	0.15	−16.54	0.02	−8.83	0.07	−0.07	0.07	−130.81	2.20	−16.33	0.29	−9.78	0.20	−1.13	0.19	−131.16	0.32	−16.64	0.01
EtOH-0.1%	−135.25	0.18	−16.46	0.04	−8.54	0.07	0.18	0.07	−112.63	8.34	−15.80	1.10	−8.19	0.23	0.18	0.37	−132.33	2.73	−16.68	0.03
EtOH-0.25%	−137.34	0.13	−16.35	0.01	−7.40	0.10	1.28	0.10	−130.63	3.32	−18.19	0.35	−10.23	1.22	−0.59	1.39	−131.62	1.96	−16.70	0.01
EtOH-0.5%	−139.15	0.31	−16.39	0.03	−6.64	0.06	2.07	0.07									−132.27	1.09	−16.69	0.01
EtOH-1.0%	−138.62	0.31	−17.34	0.04	−8.55	0.19	0.66	0.19									−133.71	5.34	−16.66	0.02
EtOH-5.0%	−131.39	0.27	−18.34	0.08	−9.19	0.16	0.54	0.16									−133.75	1.18	−16.54	0.04
EtOH-10.0%	−132.23	0.61	−22.64	0.12	−6.87	0.26	5.20	0.30									−134.39	1.61	−16.43	0.02

TABLE 2 Mean relative error (trueness) of δ^2H, $\delta^{18}O$, and $\delta^{17}O$ values from contaminated samples. Additionaly, results from different contamination identification metrics. *Z*-scores are calculated for individual isotope ratios. *Z*-score ratings are: acceptable (A), questionable (Q), or unacceptable (U). LWIA-SCI flags are: no contamination (—), narrowband contamination (NB), and/or broadband contamination (BB). ^{17}O-excess flagging is either inside the defined range = acceptable (A), indicating no problematic contamination or outside the defined range indicating problematic contamination = unacceptable (U). For $n = 5$ samples per contaminant concentration, if there is a mix of results these are recorded by result for each sample

Reference values						
Sample ID	δ^2H (‰)		$\delta^{18}O$ (‰)		$\delta^{17}O$ (‰)	
	Mean	SD	Mean	SD	Mean	SD
L-OA-ICOS reference	−132.50	0.45	−16.24	0.09	−8.81	0.10
MeOH-contaminated samples						

	Liquid OA-ICOS results							DVE-OA-ICOS results					
Sample ID	δ^2H error (‰)	δ^2H *Z*-score rating (A, Q, U)	$\delta^{17}O$ error (‰)	$\delta^{18}O$ error (‰)	$\delta^{18}O$ *Z*-score rating (A, Q, U)	LWIA-SCI flagging (NB, BB)	^{17}O-excess flagging (A/U)	δ^2H error (‰)	δ^2H *Z*-score rating (A, Q, U)	$\delta^{17}O$ error (‰)	$\delta^{18}O$ error (‰)	$\delta^{18}O$ *Z*-score rating (A, Q, U)	^{17}O-excess flagging (A/U)
MeOH-0.001%	0.80	A	0.19	0.05	A	—	A	8.94	A/QQQQ	2.28	2.22	U	U
MeOH-0.002%	0.90	A	0.34	0.27	A	—	A	7.22	A/QQQQ	3.91	2.57	U	U
MeOH-0.004%	1.15	A	0.48	0.51	AAAA/Q	NB	A	9.87	QQQ/UU	7.28	4.67	U	U
MeOH-0.008%	2.34	A	1.26	1.29	Q/UUUU	NB	U	19.06	U	15.68	9.79	U	U
MeOH-0.01%	1.05	A	2.24	1.36	U	NB	U	38.03	U	25.93	17.70	U	U
MeOH-0.016%	3.94	A	2.76	2.55	U	NB	U	38.96	U	48.92	21.82	U	U
MeOH-0.032%	8.45	Q	6.24	5.85	U	NB/BB	U						
MeOH-0.064%	17.13	U	13.09	12.64	U	NB/BB	U						
MeOH-0.1%	28.99	U	23.26	19.31	U	NB/BB	U						
MeOH-0.128%	38.17	U	30.55	24.90	U	NB/BB	U						
MeOH-0.256%	81.33	U	61.41	51.84	U	NB/BB	U						
MeOH-0.5%	157.58	U	109.81	97.49	U	NB/BB	U						
MeOH-1.0%	367.90	U	236.99	216.82	U	NB/BB	U						

(Continues)

TABLE 2 (Continued)

EtOH-contaminated samples													
	Liquid OA-ICOS results							DVE-OA-ICOS results					
Sample ID	δ^2H error (‰)	δ^2H Z-score rating (A, Q, U)	$\delta^{17}O$ error (‰)	$\delta^{18}O$ error (‰)	$\delta^{18}O$ Z-score rating (A, Q, U)	LWIA-SCI flagging (NB, BB)	^{17}O-excess flagging (A/U)	δ^2H error (‰)	δ^2H Z-score rating (A, Q, U)	$\delta^{17}O$ error (‰)	$\delta^{18}O$ error (‰)	$\delta^{18}O$ Z-score rating (A, Q, U)	^{17}O-excess flagging (A/U)
EtOH-0.001%	−1.10	A	−0.08	−0.27	A	—	A	8.43	QQQQ/U	−0.39	0.87	AA/QQ/U	AA/UUU
EtOH-0.005%	−0.90	A	−0.05	−0.36	A	—	A	4.09	A	−0.10	0.12	A	AAAA/U
EtOH-0.01%	−0.80	A	0.06	−0.19	A	—	A	9.48	AA/QQ/U	1.23	1.59	QQQ/UU	AAAA/U
EtOH-0.05%	−2.27	A	−0.02	−0.30	A	—	A	1.69	A	−0.96	−0.09	A	U
EtOH-0.1%	−2.75	A	0.27	−0.22	A	BB	A	19.87	UUUU/Q	0.62	0.44	AAA/UU	AAA/UU
EtOH-0.25%	−4.84	A	1.41	−0.11	A	BB	U	1.87	A	−1.42	−1.95	U	A/UUUU
EtOH-0.5%	−6.65	Q	2.18	−0.15	A	NB/BB	U						
EtOH-1.0%	−6.12	AA/QQQ	0.27	−1.10	Q	NB/BB	U						
EtOH-5.0%	1.11	A	−0.38	−2.10	U	BB	U						
EtOH-10.0%	0.27	A	1.94	−6.40	U	BB	U						

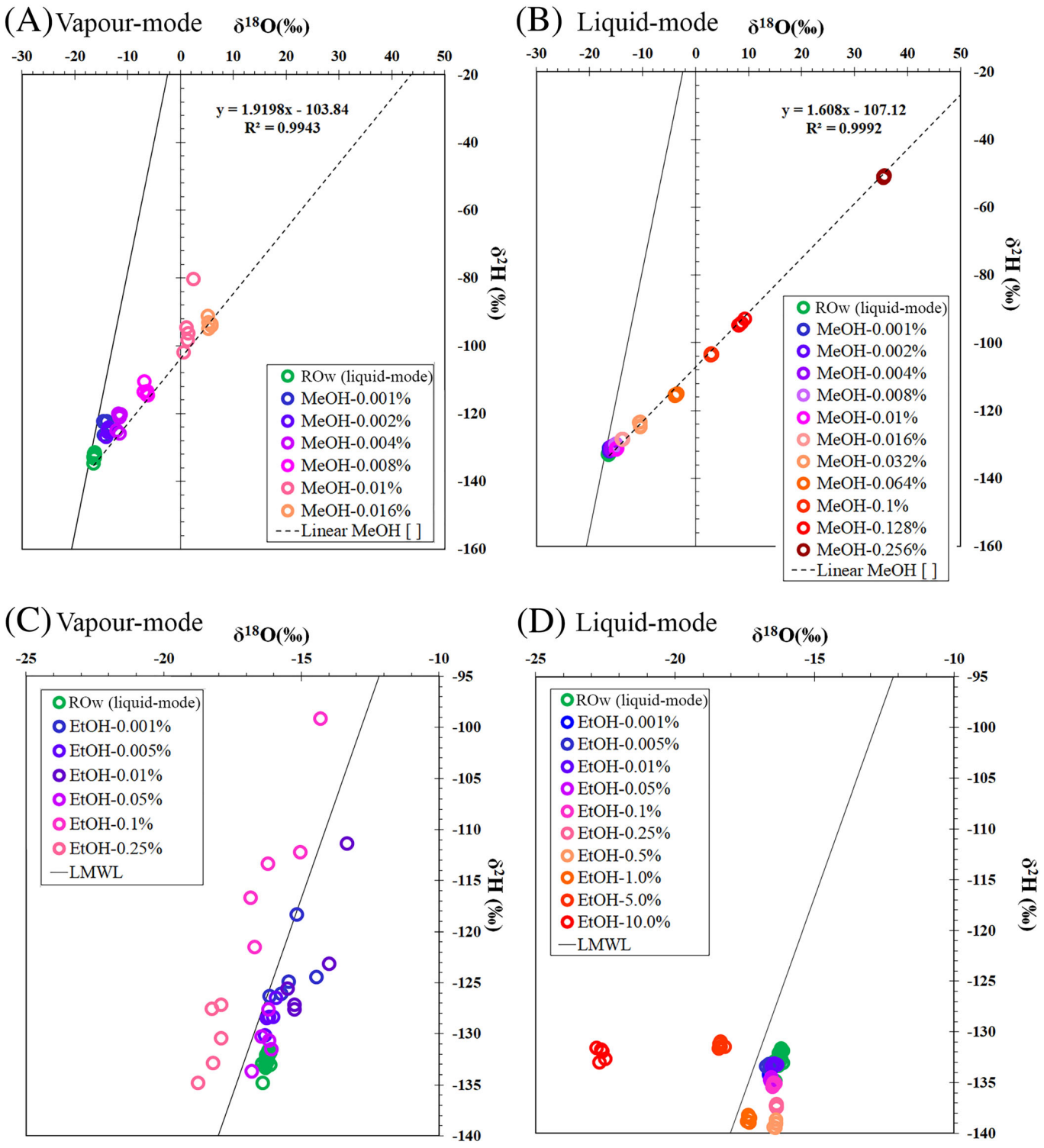

FIGURE 1 Dual-isotope plots of the stable isotope ratios produced by (A, C) vapour- and (B, D) liquid-mode analyses of (A, B) methanol-contaminated samples and (C, D) ethanol-contaminated samples ($n = 5$ per contaminant concentration). MeOH-0.5% and MeOH-1.0% results are excluded from (B) for data clarity. Local meteoric water line (LMWL) equation: $\delta^2H = 7.7 \times \delta^{18}O - 2.2‰$[47]

pronounced for vapour mode than for liquid mode (Figures 1C and 1D; Tables 1 and 2). The maximum δ^2H mean error was 19.87‰ for vapour-mode analyses and occurred at EtOH-0.1%, while the maximum $\delta^{18}O$ mean error was −1.95‰ at EtOH-0.25%. At EtOH-0.5% and higher, negative absorbance issues resulted in those vapour-mode-generated data being excluded. *Z*-scores for vapour-mode analyses were more variable than for liquid-mode analyses of ethanol-contaminated samples. At EtOH-0.005% and EtOH-0.05% the *Z*-scores fell into the acceptable range, while at EtOH-0.001%, EtOH-0.01%, and EtOH-0.1% there was a mix of acceptable, questionable,

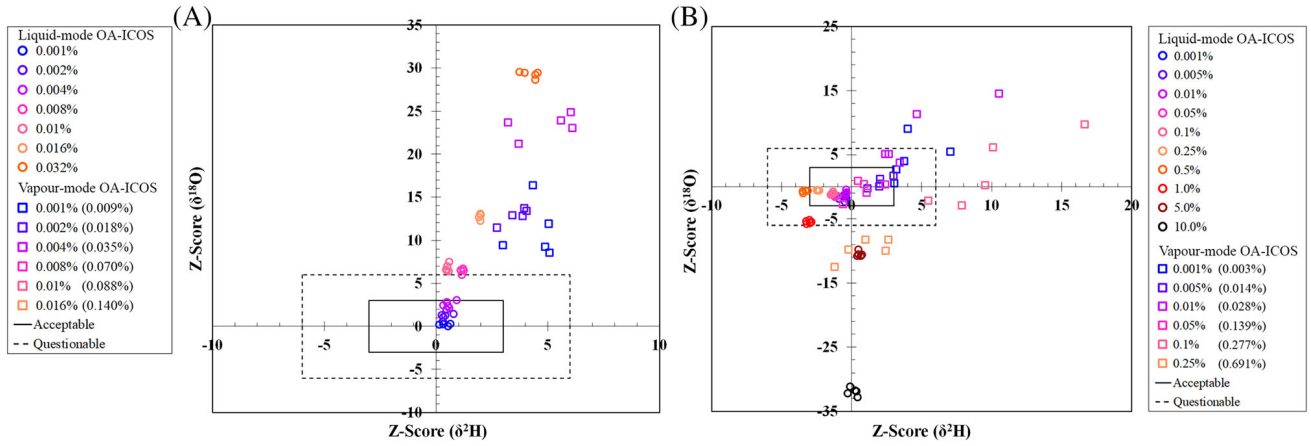

FIGURE 2 *Z*-score plots for (A) methanol-contaminated and (B) ethanol-contaminated samples analysed by vapour and liquid modes. A *Z*-score of <|3| (falling within the solid box) is considered acceptable,|3–6| (falling within the dashed box) is questionable, and >|6| (falling outside of the dashed box) is unacceptable. Vapour-mode results for methanol concentrations >0.016% and ethanol concentrations >0.25% are not included due to negative absorbance issues. Liquid-mode *Z*-scores for methanol concentrations >0.032% are not shown as the scores become so large as to obscure the plot. Concentrations in parentheses for vapour-mode data are the vapour-phase concentrations of contaminants in the analysis headspace

and unacceptable *Z*-scores. At EtOH-0.25%, all the $\delta^{18}O$ *Z*-scores were unacceptable, but all the $\delta^{2}H$ *Z*-scores fell in the acceptable range (Figure 2B).

Finally, the IRMS results had little impact from ethanol contamination. The $\delta^{2}H$ mean error had a mix of positive and negative results and the $\delta^{2}H$ value fell within ±1.89‰ of the reference ROw. The $\delta^{18}O$ mean error was only negative and $\delta^{18}O$ values fell within −0.45‰ of the reference ROw. Again, these errors were only slightly larger than the IRMS device precision ranges. All the *Z*-scores for ethanol-contaminated samples analysed via IRMS fell well within the acceptable range, except for a single data point at EtOH-1.0% where the $\delta^{2}H$ *Z*-score was questionable. Thus, for clarity, the IRMS EtOH data are not plotted in Figure 2.

3.1.3 | Differences in contamination effect for vapour- and liquid-mode OA-ICOS results

The methanol and ethanol concentrations in the vapour-phase headspace of vapour-mode samples were calculated using Raoult's law and treating the contaminant–tap water mixtures as ideal solutions. Contaminant concentrations were found to be elevated in the vapour phase relative to the original liquid concentrations (see Table 3). Table 3 also includes the liquid-mode contaminant concentrations that most closely match the contaminant concentration in the vapour-mode sample's vapour phase. These are the liquid-mode Group A results discussed below. Regarding methanol-contaminated samples, for both $\delta^{2}H$ and $\delta^{18}O$, the vapour-mode results were closer to the liquid-mode results when the liquid-mode contaminant concentration levels were comparable with the vapour-phase contaminant levels in the vapour-mode sample bags; i.e. the vapour-mode MeOH-0.001% results are closer to the liquid-mode MeOH-0.008% results than to the liquid-mode MeOH-0.001% results. This relationship was not as clear with ethanol-contaminated sample results.

For methanol-contaminated samples, the $\delta^{2}H$ and $\delta^{18}O$ values measured by vapour-mode analyses match to the higher contamination concentrations in liquid-mode analyses. For example, vapour-mode MeOH-0.001% (original liquid concentration) has a vapour-phase concentration of 0.009%, and this is comparable with the liquid-mode MeOH-0.008% contaminant concentrations. Consequently, the isotope data from vapour-mode analysis for MeOH-0.001% match more closely to liquid-mode MeOH-0.008% isotope data. The latter is observed for other methanol concentrations in Figure 3. To clarify, Figure 3 groups vapour-mode analysed isotope results with two different groups of liquid-mode results: Group A (liquid-mode-A in Figure 3) – results from samples whose contaminant concentration levels match most closely to the vapour-phase concentration of contaminants in vapour-mode samples; Group B (liquid-mode-B in Figure 3) – results from samples whose contaminant concentration levels share the same original concentration as the liquid placed in DVE sample bags. For example, the first grouping of results in Figure 3 for measured $\delta^{2}H$ values is vapour-mode MeOH-0.001% (vapour-phase concentration of methanol is 0.009%), liquid-mode MeOH-0.008% (Group A, whose contaminant concentration matches most closely to the vapour-phase contaminant concentration of vapour-mode samples), and liquid-mode MeOH-0.001% (Group B, whose contaminant concentration matches the originally prepared liquid sample contaminant concentration, placed in the vapour-mode sample bag).

The difference between mean $\delta^{2}H$ results for vapour-mode MeOH-0.001% and liquid-mode MeOH-0.001% was 8.1‰ ($p < 0.05$, using the Dunnet test) while the difference between vapour-mode MeOH-0.001% and vapour-mode MeOH-0.008% was 6.6‰

TABLE 3 Original liquid-phase concentrations of contaminant–water mixtures and their resultant calculated vapour-phase concentrations in DVE sample bag headspace. Data were calculated using Raoult's law at an analysis temperature of 22°C. The liquid-mode OA-ICOS sample concentration levels to which the DVE vapour-phase contaminant concentrations are closest are also shown

Contaminant	Contaminant concentration in DVE liquid phase (%)	Contaminant concentration in DVE vapour phase (%)	Closest liquid-mode concentration (%)
MeOH	0.001	0.009	0.008
	0.002	0.018	0.016
	0.004	0.035	0.032
	0.008	0.070	0.064
	0.010	0.088	0.100
	0.016	0.140	0.128
EtOH	0.001	0.003	0.005
	0.005	0.014	0.010
	0.010	0.028	0.050
	0.050	0.139	0.100
	0.100	0.277	0.500
	0.250	0.691	1.000

($p < 0.05$, using the Dunnet test). Similarly, for $\delta^{18}O$ data, the vapour-mode results were closer to the liquid-mode-A results than to the liquid-mode-B results.

At MeOH-0.004% the vapour-mode $\delta^{2}H$ results become statistically distinct ($p < 0.05$ using Dunnet test) from the liquid-mode-B data, but are not significantly different from the liquid-mode-A data ($p \geq 0.05$, using Dunnet test) (Figure 3). At MeOH-0.002% the vapour-mode $\delta^{18}O$ results become statistically distinct ($p < 0.05$ using Dunnet test) from the liquid-mode-B data while remaining similar to the liquid-mode-A data ($p \geq 0.05$, using Dunnet test) (Figure 3). For both the $\delta^{2}H$ and $\delta^{18}O$ values, this trend continues as the methanol concentrations increase.

The relationship described above did not occur in ethanol-contaminated sample data. We did find that ethanol concentrations were higher in the vapour-phase headspace of vapour-mode sample bags. However, the ethanol-contaminated vapour-mode results were different from those of the liquid-mode-A group data (ethanol concentration level similar to vapour-phase concentration in vapour-mode samples) and the liquid-mode-B group data (ethanol concentrations at original comparable levels) (Figure 3). We note statistically significant differences between the vapour-mode and liquid-mode-A and B results for all comparisons of ethanol samples ($p < 0.05$, using the Dunnet test) (Figure 3). The only exceptions were for the $\delta^{2}H$ and $\delta^{18}O$ results for vapour-mode EtOH-0.05%, and the $\delta^{2}H$ results for vapour-mode EtOH-0.25% where all intergroup comparisons were not statistically significant ($p \geq 0.05$, using one way ANOVA).

3.2 | Contamination detection

Contamination detection for liquid-mode OA-ICOS samples was achieved using LWIA-SCI software and the ^{17}O-excess approach. For vapour-mode OA-ICOS samples, contamination detection was carried out with the ^{17}O-excess approach only. The results of the contamination flagging are presented in Table 2.

3.2.1 | Software-based contamination detection

During liquid-mode analyses, the contamination detection software flagged methanol-contaminated samples for narrowband spectral interference at 0.004% and higher concentrations (Table 2). The isotope results for those concentrations begin to fall into the unacceptable *Z*-score range at MeOH-0.008%. Methanol concentrations of 0.128% and higher were flagged for narrowband and broadband spectral contamination. At MeOH-0.008%, MeOH-0.01%, and MeOH-0.016%, the liquid mode $\delta^{18}O$ *Z*-scores fall in the unacceptable range while the $\delta^{2}H$ *Z*-scores are acceptable. At MeOH-0.032% and higher concentrations the $\delta^{2}H$ and $\delta^{18}O$ *Z*-scores all fall into the unacceptable range. The LWIA-SCI software flagged most of the liquid-mode methanol results. Those that were not flagged (MeOH-0.001% to MeOH-0.008%) had isotope results that fell in the acceptable range, except for MeOH-0.008% which fell just outside the questionable border, into the unacceptable range.

The contamination detection software indicated broadband spectral interference in liquid-mode ethanol samples for 0.1% and higher concentrations. EtOH-0.5% and EtOH-1.0% contaminated samples were also flagged for narrowband spectral interference (Table 2). As noted above, all the liquid-mode-analysed, ethanol-contaminated samples had isotope results that fell within the *Z*-score acceptable and questionable range, except for the $\delta^{18}O$ *Z*-scores for EtOH-5.0% and EtOH-10%, which fell into the unacceptable range (Figure 2).

3.2.2 | ^{17}O-excess contamination detection

Figures 4 and 7 show the calculated ^{17}O-excess data for vapour- and liquid-mode OA-ICOS analyses of methanol-contaminated (Figure 4)

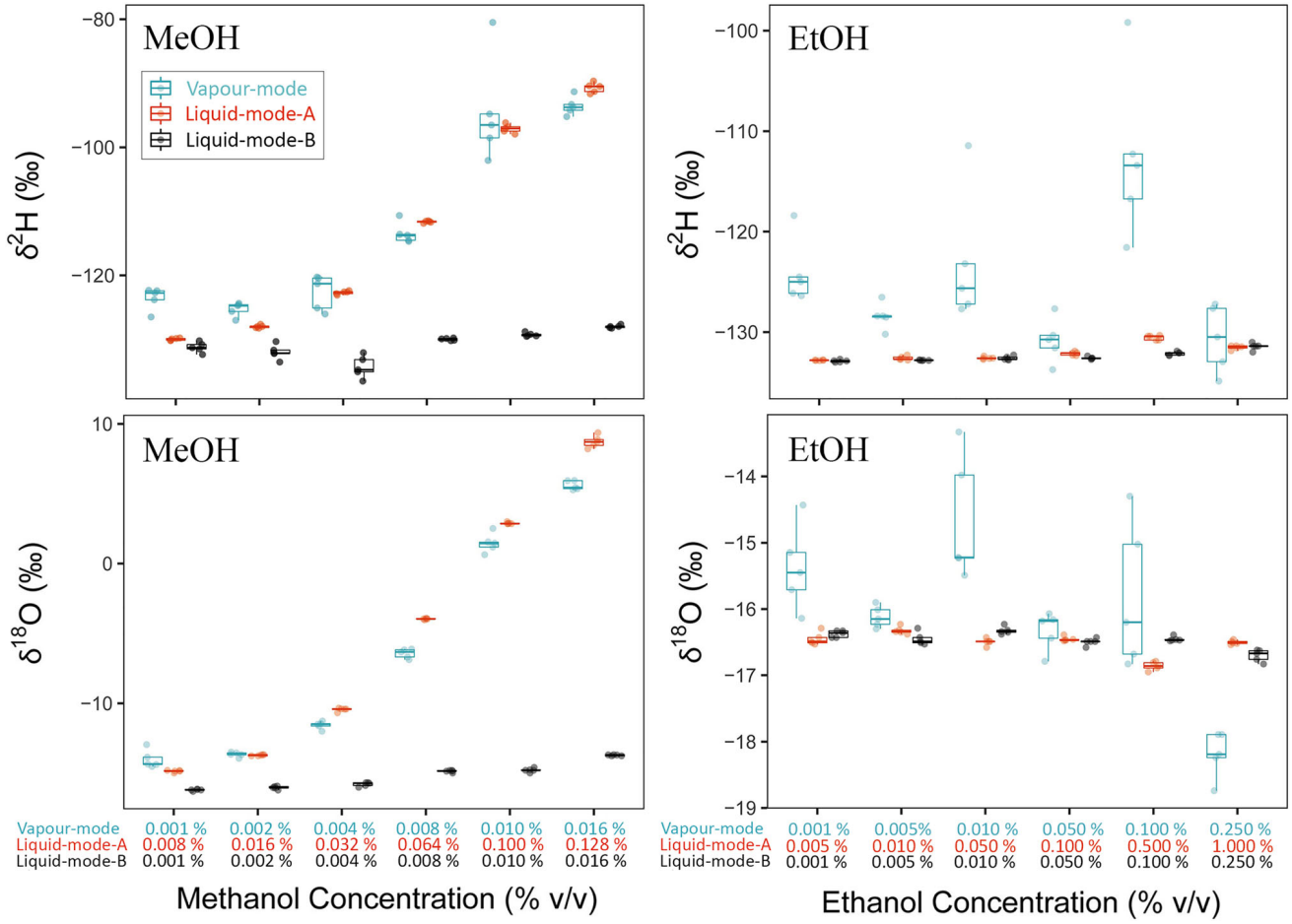

FIGURE 3 Effect of contaminants concentrating in the vapour phase of vapour-mode sample bags. Box plots of stable isotope results for contaminated samples from vapour- and liquid-mode analyses. Stable isotope results are grouped by contaminant (methanol and ethanol) and isotope ratio of interest. Box plots are grouped in sets of three: in blue, the results from vapour-mode-analysed samples; in red, the results from liquid-mode-analysed samples where the contaminant concentration is comparable with the calculated vapour-phase contamination level in vapour-mode sample bags (liquid-mode-A group); in black, liquid-mode results at contaminant concentrations that match the original liquid contaminant concentration levels of vapour-mode samples (liquid-mode-B group)

and ethanol-contaminated (Figure 7) samples. Figure 5 shows vapour- and liquid-mode results plotted in [$\delta^{18}O$, $\delta^{17}O$] space for methanol- and ethanol-contaminated samples.

Regarding methanol-contaminated samples analysed by vapour mode, the ^{17}O-excess values for isotope data at all methanol concentrations are ≥|0.43‰|, indicating the presence of problematic contamination. Indeed, all vapour-mode-analysed, methanol-contaminated samples fall into questionable and unacceptable *Z*-score ranges, indicating the effectiveness of the ^{17}O-excess metric at flagging problematically contaminated samples. The plotted $\delta^{17}O$, $\delta^{18}O$ values for all vapour-mode-analysed, methanol-contaminated samples fall outside the ^{17}O-excess detection band (see Figure 5). This band is used as a visual metric for judging contamination via the ^{17}O-excess approach. All data falling outside this band are considered to have problematic levels of contamination.

For liquid-mode analyses, the MeOH-0.001% to MeOH-0.004% results have ^{17}O-excess values that fall within the defined range of <|0.43‰|, indicating no problematic contamination. All other methanol concentrations fall outside this range, indicating problematic levels of contamination. In addition it can be seen in Figure 5 that the methanol-contaminated, liquid-mode $\delta^{17}O$, $\delta^{18}O$ data begin to fall outside the ^{17}O-excess detection band at MeOH-0.008% and higher, this being a visual indicator of sample contamination via the ^{17}O-excess approach.

The ethanol-contaminated vapour-mode sample ^{17}O-excess values provide a more variable set of results, with data falling both within and outside the defined range across all ethanol concentrations. EtOH-0.001% has 3 of 5 data points falling into the contaminated range; EtOH-0.005% and EtOH-0.01% have 1 of 5 data points falling into the contaminated range; EtOH-0.05% has all data points indicated as problematically contaminated; EtOH-0.1% has 2 of 5; and EtOH-0.25% has 4 of 5 indicated as contaminated. The ^{17}O-excess flagging for ethanol-contaminated vapour-mode samples conflicts with the *Z*-score metrics at multiple points, while agreeing at others. At EtOH-0.001% the flagged samples have mostly questionable and one unacceptable *Z*-score. At EtOH-0.005% all the

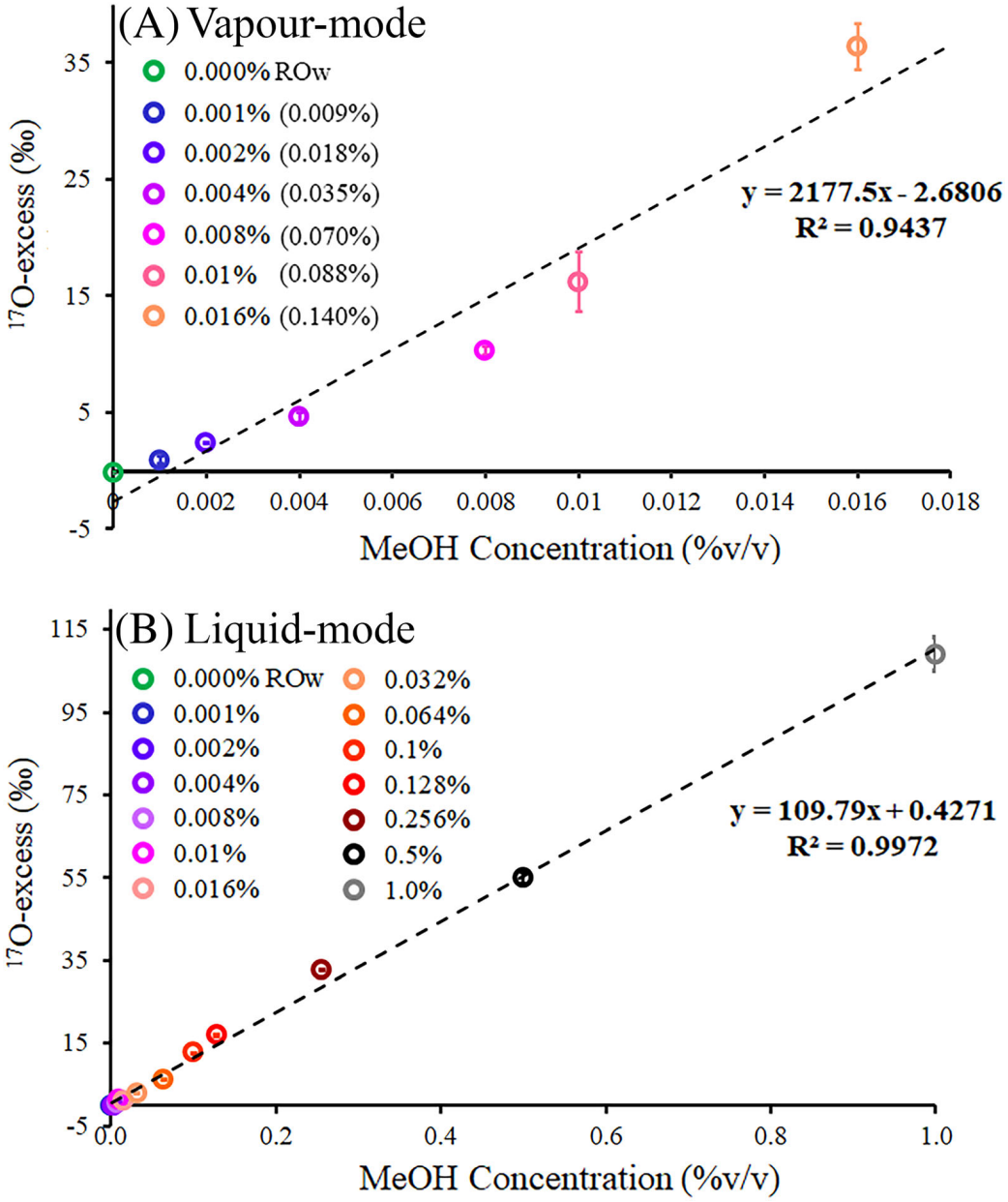

FIGURE 4 ^{17}O-excess data for methanol-induced spectral contamination effects on the measured isotopic composition of samples. Changes in ^{17}O-excess (‰) per concentration of methanol for (A) vapour-mode and (B) liquid-mode OA-ICOS analyses. Error bars show ±1 SD for $n = 5$ samples per contaminant concentration level. Concentrations in parentheses in (A) are the vapour-phase concentrations of methanol in the vapour-phase analysis headspace

Z-scores are considered acceptable while the ^{17}O-excess metric flags one data point. However, the ^{17}O-excess for this data point is −0.47‰. At EtOH-0.01% the ^{17}O-excess-flagged data point has a questionable *Z*-score, but the ^{17}O-excess metric failed to flag two data points at this concentration, both of which fall into the unacceptable *Z*-score range. At EtOH-0.05% while the ^{17}O-excess approach flagged all 5 data points, the *Z*-scores of these samples all fall within the acceptable range. At EtOH-0.1% the ^{17}O-excess flagged data points as having unacceptable and questionable *Z*-scores. Finally at EtOH-0.25% all the ^{17}O-excess-flagged data points also have unacceptable *Z*-scores.

The liquid-mode ethanol-contaminated sample ^{17}O-excess data for 0.001–0.1% concentrations are within the ^{17}O-excess detection range, indicating no problematic contamination. The ^{17}O-excess data for EtOH-0.25% to EtOH-10% fall outside the ^{17}O-excess detection range, indicating problematic contamination. For the most part the ^{17}O-excess flagging is in agreement with the *Z*-score. However, at EtOH-0.25% while all data points are flagged for contamination, the *Z*-scores are acceptable, but fall near the border of questionable. At EtOH-0.5%, the *Z*-scores are a mix of acceptable and questionable. At EtOH-1% the *Z*-scores are questionable while being flagged by the ^{17}O-excess metric. Finally at EtOH-5% and EtOH-10% the

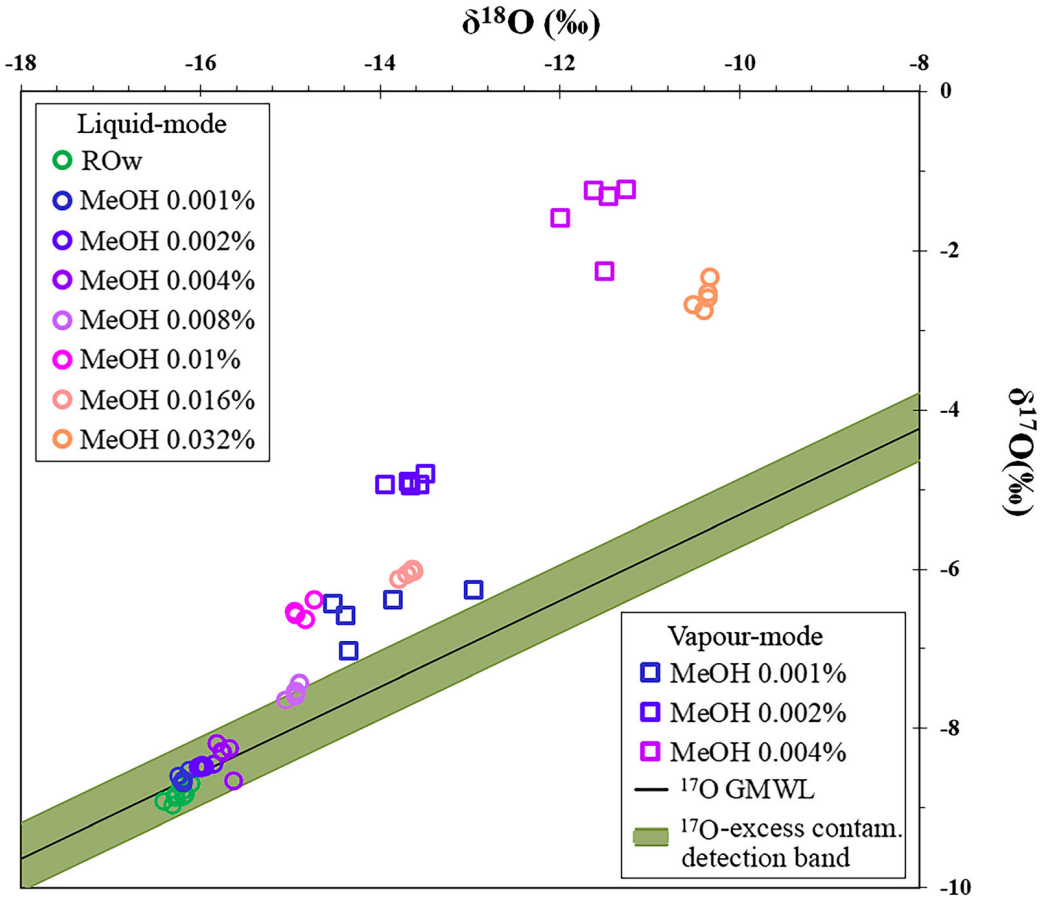

FIGURE 5 $\delta^{18}O$ and $\delta^{17}O$ data for methanol-contaminated samples from vapour- and liquid-mode analyses in [$\delta^{18}O$, $\delta^{17}O$] space. This plot is utilized as a 'visual check' for the ^{17}O-excess contamination detection approach. Data points falling within the shaded band along the ^{17}O global meteoric water line (GMWL) are considered uncontaminated. Data points falling outside the band are consider to have problematic levels of contamination. Liquid-mode data for MeOH-0.064% and higher, and vapour-mode data for MeOH-0.008% and higher are not included for clarity as these fall well away from the ^{17}O-excess detection band

Z-scores for $\delta^{18}O$ are all unacceptable while also being flagged by ^{17}O-excess.

4 | DISCUSSION

4.1 | Methanol- and ethanol-induced spectral contamination

Our results showed that methanol contamination caused larger errors in measured isotope ratios during OA-ICOS analysis and caused more results to fall into the questionable and unacceptable *Z*-score ranges than ethanol contamination. Our findings are consistent with previous work,[11,13,14,16] where the effects of methanol contamination were far more pronounced than the effects of ethanol on IRIS isotope results. We now confirm this finding for the LGR OA-ICOS system. Further, we confirm previous findings that methanol and ethanol had a limited effect on isotope results measured by IRMS.[11,13,14]

During OA-ICOS analyses (vapour and liquid modes), our data showed that isotope results skew positively in the presence of methanol contamination, as was seen in previous research.[11] Indeed, this effect is magnified with vapour-mode results relative to liquid-mode results, a finding not seen in that previous work. Previous research[14] with CRDS analysers found that the $\delta^{2}H$ and $\delta^{18}O$ errors for those data skewed in a negative direction as the methanol contamination increased. Our data further add to the body of evidence showing that methanol contamination causes a positive OA-ICOS error skew direction instead of the negative error skew for isotope results from CRDS.[11,14]

For ethanol contamination, the liquid-mode results had a mix of positive and negative errors, whereas the vapour-mode results had only positive error skew. This finding was not consistent for the OA-ICOS system's liquid analyses in a previous study,[11] where the results skewed mostly positively in the presence of contaminants. West et al[11] extracted analytes from various plants known to cause spectral contamination issues during IRIS analyses. These samples did not have their methanol and ethanol concentrations detailed, and thus a direct comparison to our work may be difficult. Our findings suggest that ethanol contamination can cause OA-ICOS results to skew in a

negative direction, but this occurred specifically only during liquid analysis. This was observed to some extent by Martin-Gomez et al[14] for the δ^2H error of the CRDS system, but less so for the δ^{18}O error related to ethanol contamination. That study detailed the effects of methanol and ethanol in water on results measured by Picarro L2120-i and L1102-i CRDS isotope analysers.[14] Their results showed that ethanol contamination caused the δ^2H error to skew in a negative direction (as seen to a small extent in our results) but that the δ^{18}O error skewed in a positive direction for the same ethanol contaminations (not seen in our results).

We agree that it is highly problematic that device-specific effects between OA-ICOS and CRDS are causing differences in the trueness (relative error) and isotopic composition of results when analysing the same contaminated samples.[11] The differences between response of the IRIS devices to contaminants are probably related to the specific range of the water absorption band of the electromagnetic spectrum being utilized by each manufacturer (Picarro CRDS and LGR OA-ICOS). In addition, the mathematical fitting procedures translating absorption into stable isotope ratios are probably unique to each manufacturer. Further collaboration between researchers and manufacturers into how these manufacturer-specific differences affect measured IRIS results should be advanced.

Our study showed that the magnitude of methanol and ethanol spectral contamination effects is not consistent between vapour- and liquid-mode OA-ICOS analyses. During vapour-mode analyses, the methanol contamination error magnitude was far greater than that seen in the liquid-mode results (Table 1). For MeOH-0.016%, the vapour-mode results were 35.01‰ (δ^2H) and 19.27‰ (δ^{18}O) more positive than the liquid-mode results for the same contaminant concentration. The MeOH-0.016% data are used for comparison here as this was the last methanol concentration that did not show evidence of negative absorbance during vapour-mode analyses. Similarly, ethanol contamination caused larger relative errors in vapour-mode results than in liquid-mode results.

The larger relative error seen during vapour-mode analysis is probably related to the volatility of methanol and ethanol. Both methanol and ethanol have lower vaporization temperatures and higher vapour pressures than water. For methanol-contaminated samples, the vapour-mode results were more similar to the liquid-mode results when using the calculated vapour-phase concentration of the contaminant than when using the original liquid concentrations for comparison. As the methanol concentrations increased, the differences between the vapour-mode and the liquid-mode results at comparable vapour-phase concentrations became smaller. However, for ethanol-contaminated samples, the vapour-mode results differed from the liquid-mode results regardless of the original or vapour-phase concentrations, as shown in Figure 3. The latter implies that ethanol contamination, while not as problematic during liquid-mode analyses, should be considered problematic during vapour-mode analyses via laser spectroscopy approaches.

Because of these effects, when using vapour-based analysis methods, plant, soil, and water samples with a potential for organic contamination should be closely monitored with available detection tools such as the ^{17}O-excess approach.[16] This is critical given the increase in vapour-mode analyses of plant and soil water through *in situ* and equilibration methods. Samples analysed via vapour equilibration approaches may be more prone to error than when using traditional liquid analysis. More research is needed to verify if the effects seen in bag equilibration approaches are observed when using *in situ* probes.

For IRMS analyses, it was found that ethanol and methanol contamination had little effect on measured results. Studies interested in water isotope analysis proficiency have used defined maximum acceptable bias values as quality thresholds.[14,45] We utilize the more strictly defined[45] maximum acceptable bias of ±2‰ for δ^2H values and ±0.2‰ for δ^{18}O values for discussion in this section. Even at high contaminant concentrations relative to the reference water, the maximum relative δ^2H error was only −2.55‰ (at MeOH-1%) and −1.89‰ (at EtOH-10%). At the same time the maximum relative δ^{18}O error was only −0.19‰ (at MeOH-1% and EtOH-10%). These values only slightly exceed the maximum acceptable bias of ±2‰ for δ^2H values, and do not exceed the maximum acceptable bias of ±0.2‰ for δ^{18}O values. This limited effect was expected and is consistent with previous findings.[14] However, that previous work showed that at EtOH-8%, the IRMS δ^{18}O error fell outside their selected maximum acceptable bias, while for EtOH-4% and EtOH-8%, the IRMS δ^2H error fell outside their selected maximum acceptable bias. We note that the differences between our IRMS results and those of other researchers[11,13,14] could be connected to the stable isotope composition of the contaminating alcohols. In addition, if those contaminating alcohols were not pure methanol or ethanol (i.e. 100% v/v) and contained some proportion of water, the isotopic composition of that water would also contribute to their IRMS measured composition. However, we note here that the methanol or ethanol would need to be at substantially high concentrations to begin to affect IRMS results. For example, given that one knows the hydrogen mole fraction (X) of the contaminating alcohol and the water with which it is mixed, as well as the δ^2H value of the alcohol and the water, the δ^2H value of the entire solution can be estimated from $\delta^2H_{sol} = (X(\text{alcohol}) \times \delta^2H(\text{alcohol})) + (X(\text{water}) \times \delta^2H(\text{water}))$. For our highest concentration of ethanol (10%) the calculated δ^2H_{sol} is −134.06‰, which is identical within error to our IRMS measured result of −134.39‰ (SD: ±1.6‰). IRMS measured the δ^2H value of our ethanol to be −179.53‰.

4.2 | ^{17}O-excess as a contaminant detector in vapour- and liquid-mode OA-ICOS analyses

Our research suggests that ^{17}O-excess values are a reliable and highly sensitive tool for detecting problematic organic contamination during OA-ICOS analyses in liquid and vapour modes, especially for samples with methanol contamination. For liquid-mode analyses, the ^{17}O-excess approach was nearly as sensitive as the LWIA-SCI detection software (1 SD ± 3‰) at indicating spectral interference for methanol samples; note that the user sets the SD setting for this software contamination detection. The SD used in this setting could be decreased to increase the sensitivity of contaminant detection by

the flagging software. While the LGR spectral contamination identifier software began indicating spectral interference at MeOH-0.004% during liquid-mode analyses, the ^{17}O-excess approach began indicating contamination at MeOH-0.008%. For liquid-mode samples at MeOH-0.004% the *Z*-scores were within the acceptable range, and the mean relative error was only 1.15‰ (δ^2H) and 0.51‰ (δ^{18}O). As the methanol concentrations rose above 0.008%, the ^{17}O-excess detection approach indicated problematic contamination in all subsequent samples, concurrent with increasing *Z*-score unacceptability and rising relative error. The ^{17}O-excess values from vapour- and liquid-mode analyses were not the same for samples of the same contaminant concentration. The vapour-mode ^{17}O-excess values were typically larger than the liquid-mode values at the same contaminant concentration. This lack of similarity for the ^{17}O-excess data between liquid- and vapour-mode analyses is probably driven by the increased concentration of contaminants in the vapour phase of vapour-mode samples, as discussed above.

For ethanol-contaminated liquid-mode analyses the contamination identifier software began noting contamination at EtOH-0.1%. However, the ^{17}O-excess approach began indicating contamination for some samples as low as EtOH-0.001%. Indeed, as noted above, in some cases the ^{17}O-excess metric flagged samples with unacceptable *Z*-scores. In other cases, however, it flagged samples with acceptable *Z*-scores and in some cases missed flagging samples with unacceptable *Z*-scores. With the wide mix of acceptable, questionable, and unacceptable *Z*-scores for ethanol-contaminated samples, even within the same concentration level it is complicated to discuss the effectiveness of the ^{17}O-excess approach and its comparison with the LWIA-SCI software. However, we note also that the software flagged liquid-mode results whose *Z*-scores fell into the acceptable ranges (EtOH-0.1% to EtOH-0.5% results).

Additionally important in this consideration is the relative error caused by ethanol. For liquid-mode samples, ethanol caused relative δ^2H errors between 0.27‰ and −6.65‰, and δ^{18}O errors between −0.11‰ and −6.4‰. While these fall outside the maximum acceptable bias of |2‰| (for δ^2H) and |0.2‰| (for δ^{18}O), the ethanol-induced errors in the δ^2H and δ^{18}O values were not nearly as large or as significant as the methanol-induced error. In samples known to have issues with contamination, methanol and ethanol are probably co-extracted in the analyte[11,12] in addition to other potential contaminating substances. From our data, it appears that the ^{17}O-excess approach is more effective at indicating methanol spectral contamination than ethanol contamination in samples. Therefore, since a mix of methanol, ethanol, and other molecules containing O-H bonds may be present in natural samples, the ^{17}O-excess approach is helpful as methanol is the more problematic of the two tested molecules for IRIS analyses.[11,13,14]

We note here crucial points on using ^{17}O-excess values as a detection tool for spectral contamination in liquid and vapour modes.

1. The *Z*-score metric is arbitrary and controlled by the chosen SD used in the calculation. Our chosen SD was 2‰ and 0.2‰ for δ^2H and δ^{18}O values, respectively, and was based on literature for liquid analyses.[45] Depending on the chosen SD a larger or smaller subset of the results would have fallen into the questionable and unacceptable *Z*-score ranges, thus impacting the chosen ^{17}O-excess threshold. This is similar to the LWIA-SCI software, wherein the user sets the acceptable SD range.
2. The acceptable ranges of δ^2H and δ^{18}O error can differ depending on the ecohydrological field of interest. Overall the data show that the ^{17}O-excess approach is highly sensitive to organic contaminants and comparable with the LWIA-SCI software in narrowband (methanol) contamination detection for liquid mode. The metrics by which a sample is considered 'contaminated' may require modification depending on the precision required by a given sampling campaign. That is, the approach should be adapted to the sampling environment. While we used a target SD (μ) defined by the International Atomic Energy Agency Isotope Hydrology Section,[45] it is essential to understand that definition

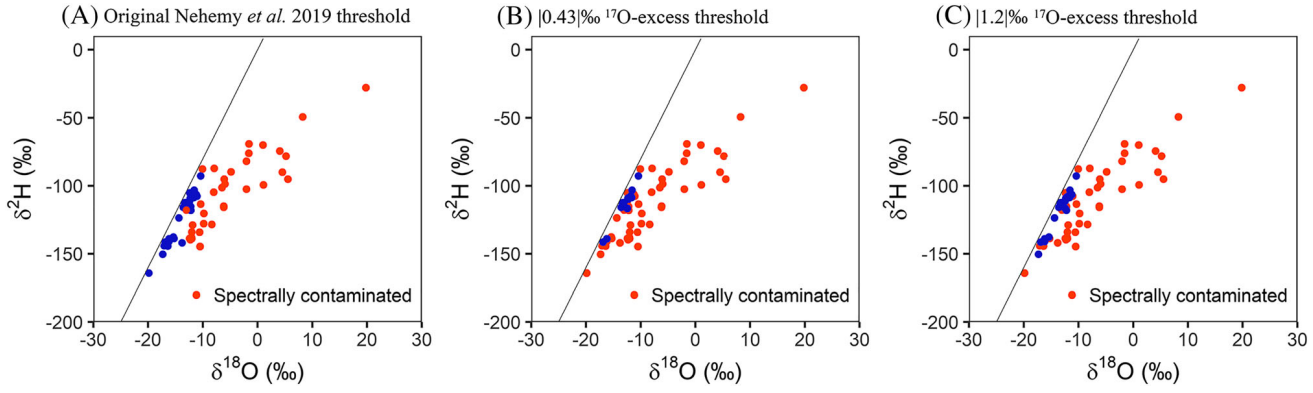

FIGURE 6 Stable isotope data from Nehemy et al[16] showing vapour-mode-analysed plant sample data. (A) The original ^{17}O-excess threshold is used. With 34 of 63 xylem samples identified as spectrally contaminated. (B) The|0.43‰| threshold is used, with the number of contaminated samples rising to 51 of 63. (C) The wider vapour-mode threshold of |1.2‰| is used, resulting in 42 of 63 samples flagged for spectral contamination

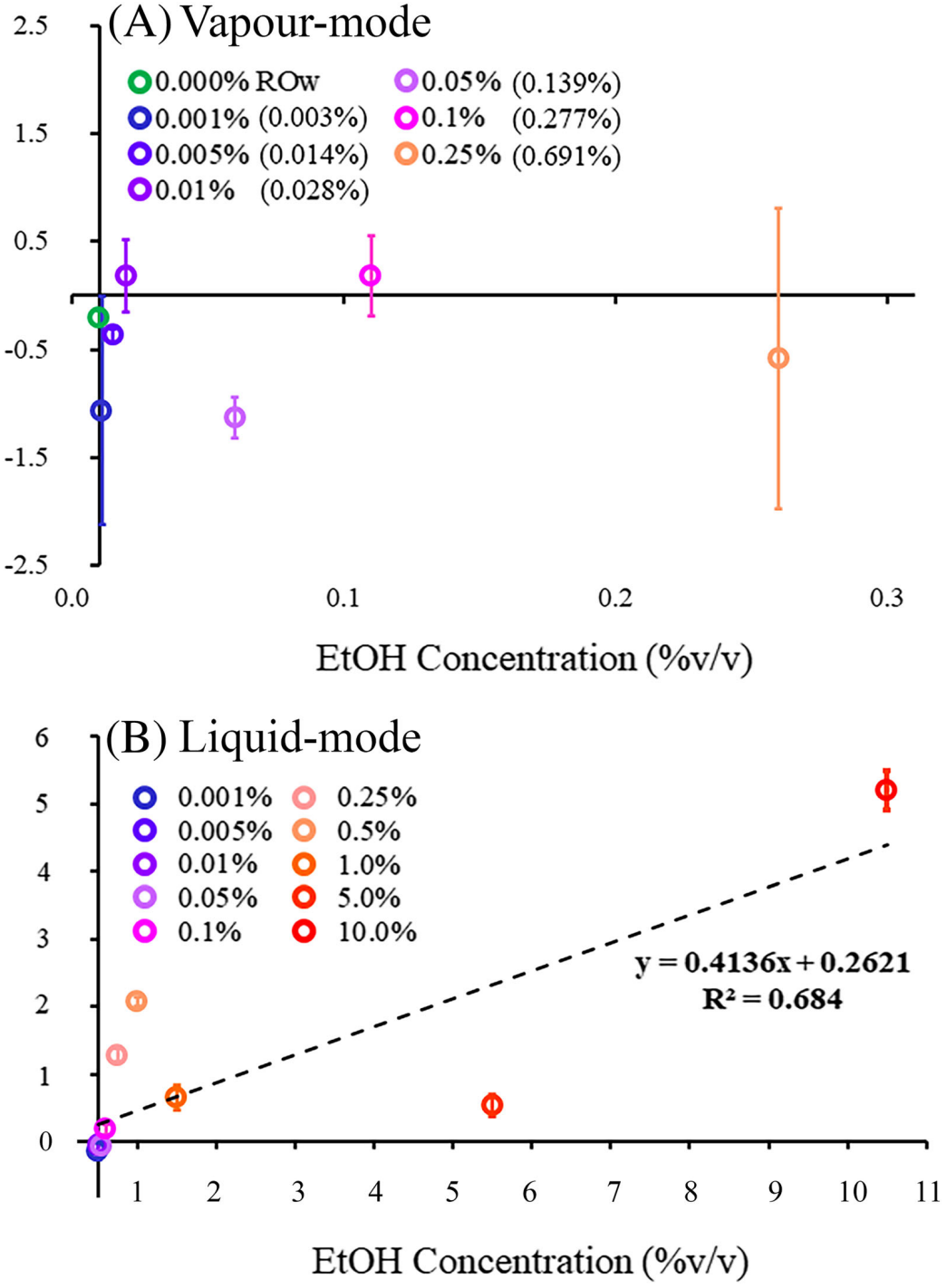

FIGURE 7 ^{17}O-excess data for ethanol-induced spectral contamination effects on the measured isotopic composition of samples. Changes in ^{17}O-excess (‰) per concentration of ethanol for (A) vapour-mode and (B) liquid-mode analyses. Error bars show ±1 SD for $n = 5$ samples per contaminant concentration level. Concentrations in parentheses in (A) are the vapour-phase concentrations of ethanol in the vapour-mode analysis headspace

was chosen for liquid-mode analyses. Previous work used a wider range of 6.0‰ for δ^2H and 0.8‰ for $\delta^{18}O^{14}$. Those values would change the ^{17}O-excess threshold to |1.2‰| for vapour mode (0.9‰ + 0.3 SD). Such a broader range of acceptable values may be appropriate for vapour-mode analyses given the larger SD of this method than for liquid-mode analyses.

4.3 | Field measurements: xylem sample assessment

In previous work,[16] the detection of xylem water spectral contamination in vapour-mode was conducted based on a spectra fit residuals plot and compared against observed soil ^{17}O-excess ranges,

given the lack of a defined ^{17}O-excess metric. In that analysis, 34 out of 63 xylem samples were identified as spectrally contaminated based on soil ^{17}O-excess values. For that xylem water dataset, if we apply the ^{17}O-excess threshold of |0.43‰| (defined by the target SD of 2‰ for δ^2H values and 0.2‰ for δ^{18}O values), the number of xylem samples in the unacceptable range increases to 51, with only 12 acceptable xylem measurements in vapour mode. If we adopt a previously used broader range as discussed above,[14] the ^{17}O-excess threshold value becomes |1.2‰| (0.9‰ + 0.3 SD). The latter is based on the MeOH-0.001% and MeOH-0.002% vapour-mode data falling into the questionable *Z*-score range with this wider target SD. Using that larger threshold the number of acceptable xylem water samples from the previous study increases to 21 acceptable and 42 contaminated (Figure 6).

4.4 | Limitations of the ^{17}O-excess contamination detection approach

The ^{17}O-excess approach is effective at indicating when methanol-driven narrowband spectral contamination corrupts results for LGR OA-ICOS analysers. However, given the weak linear relationships seen for ethanol-driven broadband spectral contamination (Figure 7), we acknowledge that this approach is not useful for indicating broadband (ethanol) contamination. Notably, ethanol contamination at low concentrations (<0.01%) did not result in large errors for liquid-mode results (Table 2). This was similarly observed in previous liquid-mode analyses of plant and water samples containing organic contaminants.[7,27] In natural plant samples we would expect a mix of methanol, ethanol, and other potential contaminating organic compounds. Given that our results confirm that methanol-driven narrowband contamination is far more problematic, the ^{17}O-excess approach is useful as a contamination flagging system.

In addition, a recent synthesis showed that leaf water samples can have substantially larger ^{17}O-excess value variation than is seen in other natural water samples.[44] The ^{17}O-excess detection approach described herein is only appropriate for measurements of soil and plant xylem samples in vapour and liquid modes. This approach would not be appropriate for leaf water samples given that they are prone to substantially larger errors. However, it may be possible to use leaf water for source water apportionment given appropriate corrections.[48] We suggest further testing of the ^{17}O-excess approach with these techniques.

4.5 | Take-home messages for users interested in plant 'water' extractions and vapour-mode IRIS analysis

The findings of our research lead us to suggest the following for IRIS users when analysing water samples extracted from plant or plant water via DVE:

1. Results generated by laser spectroscopy systems are prone to spectral interference-related errors, especially so during vapour-mode analyses. Thus, users of this approach should employ all available contaminant detection tools, although these are currently limited.
2. When analysing potentially contaminated samples, researchers can flag erroneous isotope data using contamination detection software in concert with the ^{17}O-excess approach for liquid-mode OA-ICOS analyses, and the ^{17}O-excess approach during vapour-mode OA-ICOS analyses. The LWIA-SCI software cannot currently be used for vapour-mode OA-ICOS analyses.
3. Due to the risk of contamination-driven error, data quality control is critical when using IRIS approaches to analyse plant analytes.
4. Studies should report whether a post-processing correction is applied in plant analyte results along with those post-processing errors. This information is critical for transparency in the field.

5 | CONCLUSIONS

A series of contaminant–water mixtures of varying concentrations was analysed with LGR OA-ICOS systems using two approaches: liquid mode and vapour mode. These results were compared with IRMS results for the same samples. A new spectral interference detection approach was evaluated, the ^{17}O-excess method, used during post-processing of samples.

Not surprisingly, methanol and ethanol contamination causes significant errors in measured stable isotope results. Our work confirms that methanol is a far more problematic contaminant than ethanol, causing larger relative errors in δ^2H, δ^{18}O, and δ^{17}O values during OA-ICOS analysis. While our findings are similar to previous research, the magnitude of errors, the direction of relative δ^2H and δ^{18}O trueness skew (positive versus negative), and the offsets between reference water values and contaminated sample results produced by OA-ICOS were not. The latter is probably due to a combination of factors, the foremost being the use of different IRIS methods (OA-ICOS versus CRDS). Further research into tools for contaminant detection and isotope result correction approaches for vapour-mode analysis is critically needed. While software such as the LWIA-SCI package exists for spectral interference detection during liquid water analysis by OA-ICOS, limited tools exist for use during vapour-mode OA-ICOS analyses. We found that the ^{17}O-excess approach was highly sensitive at detecting narrowband contamination in vapour- and liquid-mode OA-ICOS-analysed samples. This approach provides a sorely needed contamination detection tool for users of vapour-mode OA-ICOS.

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PEER REVIEW

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DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article and on request from the corresponding authour: CM.

ORCID

Cody Millar https://orcid.org/0000-0002-2171-581X
Magali F. Nehemy https://orcid.org/0000-0002-2212-3592
Pedro Hervé-Fernández https://orcid.org/0000-0001-6966-5690

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