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Metrological traceability of measurement results and calibration hierarchy is a prerequisite for improved data compatibility: example of the VPDB scale.

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For stable isotope data sets to be compared or combined in biogeochemical studies, their compatibility must be well understood. For $\delta^{13}\text{C}$ measurements in greenhouse gases, the WMO GAW program has set compatibility targets of 0.010 ‰ for atmospheric CO_2 and 0.020 ‰ for atmospheric methane (in background air studies [1, 2]). The direct comparison of samples between laboratories can provide limited information, such as a snapshot for a specific time period, but combining data sets produced over decades requires more efforts. To produce high quality data, reliable calibrations must be made, mutually consistent values of reference materials (RMs) must be used, and a traceability scheme that ensures low uncertainty must be implemented.

The VPDB $\delta^{13}\text{C}$ scale provides example of approaches developed recently. Several problems with the existing implementation of the VPDB scale have been identified between 2009-2016 [3]: the primary reference material (RM) NBS19 was exhausted and needed to be replaced; the $\delta^{13}\text{C}$ of LSVEC (used to anchor the VPDB scale at negative $\delta^{13}\text{C}$) was found to be drifting and its use as a RM for $\delta^{13}\text{C}$ was discontinued [4]; other RMs that were available in 2016 (e.g., NBS18) were not able to be used to develop new RMs as their uncertainties were too large. Given that the VPDB scale is artefact-based and not supported by absolute ratio measurements with uncertainty as low as required, the principles of value assignments on the VPDB scale were needed to be revised.

To ensure that a revised scheme did not encounter similar problems (with dependence on a single scale-anchor), several fundamental metrological principles were considered: (i) traceability of measurement results to the primary RM, (ii) a hierarchy of calibrators and (iii) comprehensive understanding of measurement method(s) [5]. The revised VPDB scheme [3] was applied to the new primary RM [6] and three RMs covering a large $\delta^{13}\text{C}$ range (to negative values) [7]. Values were assigned in a mutually consistent way, with uncertainties ranging from 0.010 to 0.015 ‰, depending on the assigned $\delta^{13}\text{C}$. Each RM value has an uncertainty assigned that includes all known instrumental corrections, potential alterations due to storage, and inhomogeneity assessment [6,7]. The scheme allows for the $\delta^{13}\text{C}$ range to be expanded by developing new carbonate RMs, and to be extended to matrix-based RMs.

The revised VPDB $\delta^{13}\text{C}$ scale realization should lead to a robust basis for improving data

compatibility. The developed framework can be applied to other measurements of biogeochemical interest, such as small ^{17}O variations (in H_2O , carbonates and other samples), clumped isotopes, and various paleoclimate reconstructions. Notably, the traceability principle is helpful in realistic uncertainty estimations which provide a tool to understand constrains and limiting steps in data comparisons.

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