Results of a Long-Term International Comparison of Greenhouse Gas and Isotope Measurements at the Global Atmosphere Watch (GAW) Observatory in Alert, Nunavut, Canada

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Abstract

Since 1999, Environment and Climate Change Canada (ECCC) has been coordinating a multi-laboratory comparison of measurements of long-lived greenhouse gases in whole air samples collected at the Global Atmosphere Watch (GAW) Alert Observatory located in the Canadian high Arctic (82°28' N, 62°30' W). In this paper, we evaluate the measurement agreement of atmospheric CO_2, CH_4, N_2O, SF_6, and stable isotopes of CO_2 ($\delta^{13}C$, $\delta^{18}O$) between leading laboratories from 7 independent international institutions. The measure of success is linked to target goals for network compatibility outlined by the World Meteorological Organization's (WMO) GAW greenhouse gas measurement community. Overall, based on ~8000 discrete flask samples, we find that the co-located atmospheric CO_2 and CH_4 measurement records from Alert by CSIRO, MPI-BGC, SIO, UHEI-IUP and ECCC, versus NOAA (the designated reference laboratory) are generally consistent with the WMO compatibility goals of ±0.1 ppm CO_2 and ±2 ppb CH_4 over the 17-year period (1999 – 2016), although there are periods where differences exceed target levels and persist as systematic bias for months or years. Consistency with the WMO goals for N_2O, SF_6, and stable isotopes of CO_2 ($\delta^{13}C$, $\delta^{18}O$) has not been demonstrated. Additional analysis of co-located comparison measurements between CSIRO and SIO versus NOAA or INSTAAR (for the isotopes of CO_2) at other geographical sites suggests that the findings at Alert for CO_2, CH_4, N_2O and $\delta^{13}C$-CO_2 could be extended across the CSIRO, SIO, and NOAA observing networks. The primary approach to estimate an overall measurement agreement level was carried out by pooling the differences of all individual laboratories versus the designated reference laboratory and determining the 95th percentile range of these data points. Using this approach over the entire data record, our best estimate of the measurement agreement range is -0.51 to +0.53 ppm for CO_2; 0.09 to +0.07 ‰ for $\delta^{13}C$; -0.50 to +0.58 ‰ for $\delta^{18}O$; -4.86 to +6.16 ppb for CH_4; -0.75 to +1.20 ppb for N_2O and -0.14 to +0.09 ppt for SF_6. A secondary approach of using the average of 2 standard deviations of the means for all flask samples taken in each individual sampling episode provided similar results. These upper and lower limits represent our best estimate of the measurement agreement at the 95% confidence level for these individual laboratories, providing more confidence for using these datasets in various scientific applications (e.g., long-term trend analysis).

1. Introduction

81 For more than 60 years, scientists have been making high-precision measurements of

82 atmospheric CO_2 [**Keeling, 1960**]. At first, the objective was to understand global features in

83 well-mixed marine air by documenting CO_2 abundance, seasonal patterns, and trends. For

84 this purpose, only a few remote sampling sites were established. Over time the emphasis

85 has shifted to better understand the carbon cycle including emissions to and removal

86 processes from the atmosphere. Today, a global observational network maintained by many

87 laboratories operates high-precision measurements of long-lived greenhouse gases (GHGs)

88 and complementary trace species at hundreds of locations [**WMO, 2019, 2022**]. The

89 measurement community has held regular meetings on measurement technology since

90 1975, initiated by Charles David Keeling. Proceedings from these meetings are published in

91 GAW reports [e.g., **GAW Report #229; 242; 255**], which are important references for

92 existing and new laboratories. These reports include measurement target recommendations

93 for GHG network compatibility. These targets reflect the scientifically desirable level of

94 network agreement in measurements of well mixed background air so the data of different

95 laboratories can be used together in global models or to infer regional GHG fluxes.

96

97 Atmospheric measurements of CO_2 and other trace gas species and isotopes are reported

98 by many international laboratories and are often freely available either directly from the

99 originating measurement laboratory [**Masarie et al., 1995, 2014, Ramonet et al., 2020,**

100 **Heimann et al., 2022**] or from the WMO World Data Centre for Greenhouse Gases-

101 (WDCGG) [**https://gaw.kishou.go.jp**]. For nearly 30 years, atmospheric measurements of

102 CO_2 have been used to derive estimates of CO_2 surface fluxes around the globe [**Heimann**

103 **and Keeling, 1989; Tans et al., 1990; Fan et al., 1998; Bousquet et al., 2000; Gloor et al.,**

104 **2000; Gurney et al., 2002; Peters et al., 2007; Chevallier et al., 2010; Peylin et al., 2013;**

105 **Rödenbeck et al, 2018a, 2018b; Friedlingstein, et al., 2022**]. Similar studies have also

106 been carried out for CH_4 [**Houweling et al., 2017**] and N_2O [**Schilt et al., 2010; Thompson**

107 **et al., 2019**]. When all available datasets are used in those applications the users usually

108 assume that these datasets are compatible and consistent over time. However, the

109 applications may be limited by various types of inconsistencies between the datasets,

110 including differences in scales or scale realizations and in sampling systems or procedures

111 etc. When persistent bias exists between laboratories, the applications such as flux

112 estimates derived by modelling systems using combined datasets on various spatial domains

113 and temporal scales can have large uncertainties [**Masarie et al., 2001; Ramonet et al.,**

114 **2020**]. To address potential bias, laboratories routinely evaluate measurement traceability

115 and reproducibility within their own laboratory and also compare their measurements with

3

116 those from other laboratories. Data providers in the measurement community are working

117 hard to include uncertainties with their measurements in order to inform data users. For

118 these reasons, evaluating and quantifying the inconsistencies/or biases/ or level of

119 agreements for observational records within and between laboratories over time is important.

120

121 The widely adopted strategy for assessing the level of agreement of different atmospheric

122 trace gas data-records is to conduct ongoing comparisons of the measurements of flask air

123 collected at the same time and the same location [**Masarie et al., 2001; Masarie et al.,**

124 **2003; Langenfelds et al., 2003**]. Based on these previous studies**,** which involved the

125 comparison of only two laboratories at the same location, this comparison strategy can

126 reveal differences from air sample collection, storage, extraction and analysis, data

127 processing, and maintenance of the laboratory calibration scale etc. Subtle problems can

128 arise at any step in the measurement procedure. They can occur simultaneously and may

129 exist in one or more of the participating laboratories. Identifying the cause(s) of these

130 inconsistencies often proves difficult [**Masarie et al., 2001**]. Many laboratories often

131 participate in additional comparison experiments designed to help elucidate the cause(s) of

132 observed differences. Laboratories also realize that when comparison results are examined

133 in near real-time, the information can be a valuable quality control measure where problems

134 can potentially be detected and addressed soon after they develop [**Levin et al., 2020**]. A

135 data comparison site administered by NOAA and accessible exclusively to data providers,

136 was established for on-going comparisons in 1999 and it continues operating today. This

137 platform provides preliminary comparisons for quality control purposes and serves as a good

138 starting point for further in-depth analysis.

139

140 The Alert Observatory (ALT), Canada, along with the Mauna Loa Observatory (MLO), USA,

141 and the Cape Grim Observatory (CGO), Australia, are designated as GHG comparison sites

142 by WMO-GAW **[GAW Report #168]**, where well-mixed background air can be sampled and

143 measured. Alert has the most extensive flask comparison program of the three with seven

144 individual flask programs at any time, each focusing on a variety of measurements and

145 respective scientific priorities. In addition**,** the corresponding comparison results among the

146 three sites (ALT, MLO & CGO) can provide more information on site-specific inconsistencies

147 and facilitate merging the data records from individual networks.

148

149 In this paper, we present the comparison results of atmospheric CO_2, CH_4, N_2O, SF_6, and the

150 stable isotopes of CO_2 ($\delta^{13}C$, $\delta^{18}O$) measured by the 7 international institutions at Alert over

151 the period of 1999-2016. Although some laboratories have measurements prior to 1999 and

152 continue after 2016, this period was chosen because it includes the largest number of

153 laboratories and species measured. The participating institutions are Environment and

154 Climate Change Canada (ECCC), Commonwealth Scientific and Industrial Research

155 Organisation (CSIRO), Max Planck Institute for Biogeochemistry (MPI-BGC), Heidelberg

156 University, Institut für Umweltphysik (UHEI-IUP), Laboratoire des Sciences du Climat et de

157 l'Environnement (LSCE), Scripps Institution of Oceanography (SIO), and the National

158 Oceanic and Atmospheric Administration (NOAA) in collaboration with the Stable Isotope

159 Laboratory at the University of Colorado Institute of Arctic and Alpine Research (INSTAAR).

160 Together with Alert results, we also present corresponding comparisons between CSIRO,

161 SIO and NOAA at MLO and between CSIRO and NOAA at CGO for the same time period

162 (1999-2016). This is the first report of such a large-scale comparison study. While timely

163 publications of the inter-comparison results are desirable, it can be challenging due to the

164 large number of groups involved and on-going evolving parameters including the adoption of

165 new calibration scales, data corrections and the limited dedicated resources to carry out

166 these exercises.

167

168 **2. Methods**

169

170 **2.1 Types of Comparison**

171

172 The commonly used measurement approaches for GHGs and related tracers include 1)

173 discrete flask air samples collected in the field (commonly collected as a pair or as multiple

174 flasks in series or in parallel) and shipped to a measurement laboratory or laboratories for

175 analysis, and 2) continuous measurements in situ, conducted using analytical equipment

176 located at the sampling location. The two approaches are complementary, and each

177 approach will remain essential due to their respective advantages and disadvantages. In situ

178 measurements can provide information at very high temporal resolution so that synoptic

179 scale meteorological events can be observed, which may only by chance be captured by a

180 weekly discrete air sample. In situ monitoring approach requires a physical facility with

181 reliable power, easy access as well as a high degree of automation and internet capability to

182 monitor the observation systems remotely. On the other hand, flask air samples are returned

183 to the laboratories with sufficient air and many laboratories can measure multiple trace gases

184 and their stable isotopes from a single discrete air sample. Also, the relatively low operating

185 cost and minimal infrastructure requirements of flask sampling allows for spatial coverage

186   involving more locations. Many laboratories have opted for an approach including discrete

187   flask-air sampling and, when possible, in situ measurements at one or two key sites to

188   balance temporal and spatial coverage and a suite of measured species.

189

190   This study presents two types of discrete flask comparisons, which are known as co-located

191   and same-flask comparisons. The focus is the co-located comparisons but results from the

192   same-air flask comparisons, as well as same-cylinder (Round Robins) comparisons, are

193   included to help facilitate the interpretation of the co-located comparison results. These

194   complementary comparisons could reveal cumulative differences due to errors introduced at

195   one or more steps in the entire sampling and measurement process.

196

197   ***Co-located flask air measurement comparison***: A co-located comparison generally

198   describes a comparison of two or more measurement records derived using independent

199   collection systems or methods and/or analytical systems at the same location, at

200   approximately the same time and during predefined atmospheric conditions (i.e. wind

201   direction and minimum wind speed requirements). When these conditions are met, observed

202   differences are primarily due to experimental discrepancies instead of changes in the

203   atmospheric signal. Co-located comparisons are designed to evaluate the measurement

204   agreements within or between laboratories due to uncertainties associated from sampling

205   procedures/systems, analytical procedures, data processing, and laboratory calibration

206   scales. Potential errors could arise from any or all of the steps.

207

208   ***Same-flask air measurement comparison***: A same-flask air comparison evaluates the

209   independent measurement results when two or more programs or analytical systems

210   measure air from the same "collected sample" container for the same suite of trace species.

211   Typically, the same-flask air comparison sample is shipped from the remote sampling

212   location to the closest participating laboratory or to the laboratory with lowest sample

213   consumption. This same-flask sample is then shipped to a second participating laboratory

214   for analysis. Additional laboratories or analytical systems could further analyze the sample

215   provided there is sufficient air remaining in the flask, although the risk of sample

216   contamination or alteration may increase. A same-flask comparison experiment evaluates

217   the measurement agreement within or between laboratories caused only by measurement

218   and data processing steps and not by sample collection procedures/systems. A problem

219   during sample collection, such as contamination, could still potentially affect the air in the

220   flask, but this should not impact the comparison results for same-flask analysis. Typically,

221 only one flask of a pair is analyzed by both labs, thereby providing information whether the
222 analysis procedure by one of the labs has caused contamination or altered the composition
223 of the air in the flask. The reference laboratory for same-flask comparisons at Alert is ECCC.
224
225 ***Same-cylinder air measurement comparison***: A same-cylinder air measurement
226 comparison refers to an experiment in which two or more laboratories measure air in a
227 pressurized cylinder for the same suite of trace species and then compare the independent
228 measurement results. Like the same-flask air comparison experiment, the same-cylinder air
229 comparison evaluates the measurement agreements within or between laboratories involving
230 the overall uncertainties from analytical procedures (i.e., extracting air from the cylinder,
231 introducing the aliquot of air into their detection system, measuring the sample) to processing
232 the results and maintaining their laboratory calibration scales. Because the volume of air
233 sample in a pressurized cylinder is orders of magnitude greater than that in a flask, many
234 more laboratories can participate in the comparison, and each laboratory can make multiple
235 measurements thereby obtaining an optimized measurement uncertainty. One drawback of
236 the same-cylinder comparison is the added time and expense of shipping pressurized
237 cylinders, which can be subject to strict international safety regulations. Consequently, the
238 frequency for this type of comparison is from quarterly, at best, to every few years and the
239 results only represent a snapshot in time. It should be noted that analyzers used to measure
240 flask samples are not necessarily the same instruments that are used for cylinder air analysis
241 in each laboratory, and this can contribute uncertainty and possibly bias to the comparison.
242 It is important in these types of comparisons that at least one laboratory, generally the
243 coordinating laboratory, measure the air before and after any other laboratories to
244 characterize/quantify any composition changes that may have occurred during the period of
245 comparison. In addition, it is important to note that drifts in concentrations may occur with
246 cylinder depressurization.
247
248 The WMO/IAEA "Round Robin" (RR) comparison experiment, administered by NOAA, is one
249 example of a same-cylinder air comparison experiment. This experiment is designed to
250 assess the level of agreement within the participating laboratories and assess their ability to
251 maintain links to the WMO mole fraction scales for CO_2, CH_4, and other trace gas species.
252 There have been seven WMO/IAEA Round Robin experiments since first introduced in 1974;
253 the most recent experiment started in November of 2020, includes participation by 59
254 laboratories [Global Monitoring Laboratory - Carbon Cycle Greenhouse Gases (noaa.gov)]
255 and is still ongoing. Round Robin results from RR# 5 and 6 from the participating

laboratories are included in certain figures and in **Table S1**, if the results are on the same scale as the data used in this analysis**.**

2.2 The Alert Dr. Neil Trivett Global Atmosphere Watch Observatory

Alert, Nunavut, is located on the northern tip of Ellesmere Island in the high Canadian Arctic (82°28' N, 62°30' W) far from the major industrial regions of the Northern Hemisphere. Alert is the site of a military station, Canadian Forces Station (CFS) Alert, and an ECCC Upper Air Weather Station. The Alert Dr. Neil Trivett Global Atmosphere Watch (GAW) Observatory (ALT) is located 6 km south of CFS Alert on a plateau 210 m above sea level. The land around Alert is covered with snow for almost ten months of the year and has a sparse covering of polar desert vegetation in the summer. The degree of contamination from the local environment is minimal, with winds originating from within the ENE sector, which includes CFS Alert camp [**Worthy et al., 1994**], less than 4% of the time. The ALT observatory is ideally situated for monitoring well-mixed air masses representative of very large spatial extent in the Northern Hemisphere. ALT has been the cornerstone of ECCC's atmospheric research program since 1975, and in 1986, was officially designated a WMO/GAW Global Observatory. The Observatory was officially renamed to the Dr. Neil Trivett Global Atmosphere Watch Observatory in 2006. With its existing infrastructure and strong multi-laboratory research activity, ALT is well positioned to support a multi-laboratory co-located atmospheric comparison experiment.

2.3 Flask Sampling at ALT, MLO and CGO

2.3.1 Sampling timelines

The species measured, types of comparisons (co-located / same flask), and timelines of comparison experiments conducted at Alert from 1999-2016 are summarized in **Table 1**. Individual laboratory participation and species measured were not consistent over the entire 17-year period. For example, ECCC's program for CO_2 isotopes was terminated in December 2009 and LSCE's program for all trace gases and isotopes was discontinued in September 2013. The same flask air comparison program for all trace gases at Alert has an end date of December 2013.

At MLO and CGO, co-located flask sampling was conducted by CSIRO, SIO and NOAA for the same species and similar time periods as ALT.

290

2.3.2 Sampling systems

Table 2.1 describes the sample collection system at ALT for each laboratory, including flask type, sampling frequency and apparatus used during the specified time period. Most laboratories at ALT used double-stopcock flasks, which allow for flow-through flushing prior to filling to an overpressure of 5 to 15psi. Exceptions include SIO, who used single-stopcock, evacuated flasks and CSIRO, who used some single-stopcock pressurized flasks from 1999 to 2003. Air was typically dried using a cryocooler before filling by most laboratories, except SIO and NOAA, who didn't dry their air samples either by a cryocooler or by a chemical drier, and MPI-BGC, who used a $Mg(ClO_4)_2$ dryer until 2015 before switching to a cryocooler. Sampling was conducted at a height of 10m, except SIO and NOAA, whose intakes were roughly 2m and 5m, respectively.

At MLO, SIO's sampling was the same as ALT, but CSIRO's sampling used a chemical dryer instead of a cryocooler and had a 40m air intake. NOAA's sampling was similar to ALT, but some samples were also taken via an undried flow from their *in situ* system (40m). [**Conway et al., 1994** and **Dlugokencky et al., 1994**]**.**

At CGO, CSIRO's sampling used a chemical dryer from 1999 to 2014 and then switched to a cryocooler and new sampling system. NOAA's sampling at CGO was partially dried, in contrast to being undried at Alert. Samples from both laboratories were taken from 70m heights. [**Francey et al., 2003**] and [**Langenfelds et al., in press**]. **Table 2.2** outlines the various differences between sampling at ALT, MLO and CGO for CSIRO, SIO and NOAA. Further details about the sampling procedures of all laboratories can be found in the Supplementary material (SI). Notable impacts of certain sampling parameters on the results, are mentioned in the Results and Discussion (section 3).

2.3.3 Sampling conditions

Table 3 provides the coordinated ALT weekly flask air collection schedule for participating laboratories. The coordinated sampling schedule was devised to ensure that the flask samples for each individual laboratory are collected on the same day and as close in time as possible, within a 2-hour window. Small variations in sampling time are unlikely to result in notable discrepancies. Flask air samples were collected at Alert during persistent southwesterly wind conditions, when wind speeds were greater than 1.5 m s^{-1} for several hours prior to sample air collection. If conditions were unsuitable on the regular sampling

324 day (Wednesday), sampling would be postponed to the following day. If conditions remained

325 unfavorable by Friday, sampling would proceed, but it was acknowledged that conditions

326 were suboptimal.

327 At MLO, sampling for all laboratories (NOAA, CSIRO and SIO) was conducted within an hour

328 of each other and prior to noon (local time) in an effort to avoid upslope, non-baseline wind

329 conditions at the site.

330 At CGO for NOAA and CSIRO, sampling was predominantly carried out under baseline

331 conditions of 190-280°N wind direction and wind speeds exceeding 5 ms^{-1} wind speed, or the

332 data was subsequently filtered for baseline conditions.

333

334 **2.4 Instrumentation and Analytical Methods**

335

336 Instrumentation and methods used to measure the flask air samples collected at the

337 sampling sites vary between the laboratories and continue to evolve within each laboratory.

338 To the extent possible, each laboratory handles the flask air samples and measurements in

339 the same way as other flasks from their observing network. **Table 4** summarizes each

340 laboratory's analytical instrumentation and calibration scales used for each species, for the

341 period of this study. A brief summary of the instrumentation is provided below and calibration

342 scales will be discussed in more detail in the results and discussion (section 3).

343

344 For CO_2, all laboratories except for NOAA and SIO used gas chromatography (GC) equipped

345 with a nickel catalyst and flame ionization detector (FID) for the analysis of CO_2 in the flask

346 air samples. The nickel catalyst converts CO_2 in the sample to CH_4, permitting analysis of

347 CO_2 using the FID. NOAA used non-dispersive infrared (NDIR) spectroscopy throughout and

348 SIO used an NDIR until 2012, and then switched to a Cavity Ring Down (CRDS) analyser.

349 The GC, NDIR and CRDS systems have comparable analytical precision, ranging between

350 0.01 ppm (CRDS) and 0.05 ppm (GC).

351

352 For stable isotope ratio measurements of atmospheric CO_2, all participating laboratories

353 used Isotope Ratio Mass Spectrometry (IRMS). Before introduction of the sample into an

354 IRMS, the CO_2 in the air sample is first extracted using either an off-line glass vacuum

355 extraction system to prepare samples for later analysis [**Bollenbacher et al., 2000; Huang

356 et al., 2013**], or using an on-line metal vacuum extraction system coupled directly to the

357 mass spectrometer [**Trolier et al., 1996; Werner et al., 2001; Allison and Francey 2007**]

358   for analysis within 1 hour of CO_2 extraction. All laboratories except ECCC and SIO used an

359   on-line extraction approach; ECCC and SIO used an off-line technique where pure CO_2

360   samples were flame-sealed in ampoules after extraction and stored for variable lengths of

361   time, ranging from one month to one year before IRMS analysis (it has been verified at

362   ECCC that the isotopic compositions of CO_2 in ampoules do not change within the range of

363   accepted uncertainty during a storage time of > 10 years). All the laboratories used dual-

364   inlet mode for $\delta^{13}C$ and $\delta^{18}O$ measurements but employed different strategies to link the

365   individual sample measurements to the primary scale VPDB-CO_2. **Table 5** details the various

366   calibration strategies used and highlights the differences that exist between the laboratories.

367   Since 2015, the WMO-GAW community has endorsed the JRAS-06 realization [**Wendeberg**

368   **et al., 2013, WMO, 2011; GAW#194**] of the VPDB-CO_2 scale for reporting stable isotope

369   measurements of atmospheric CO_2, but this has not been fully implemented by all

370   laboratories. For each laboratory, the repeatability of $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 measurements

371   are typically less than 0.02‰ and 0.04‰ (one-sigma), respectively.

372

373   For CH_4, all participating laboratories used gas chromatography (GC) with flame ionization

374   detection (FID) for analysis of CH_4, with typical analytical repeatability of less than 3 ppb.

375   For N_2O and SF_6, all participating laboratories used gas chromatography (GC) equipped with

376   an electron capture detector (ECD) for analysis of N_2O and SF_6 in the weekly collected flask

377   air samples. The analytical repeatability for N_2O and SF_6 using GC-ECD is typically 0.2 ppb

378   and 0.04 ppt respectively.

379

380   **2.5 Data Preparation**

381

382   All measurements used in this study have been screened by the originating laboratory to

383   ensure that each sample and subsequent measurement have not been compromised during

384   collection, storage and analysis. Each laboratory determines their own criteria for the quality

385   control of their data and assigns the flags "valid", "invalid" or "suspected". These data files

386   were provided to us by individual laboratories and have specific time stamps, which can be

387   found in **Table S2**. These time stamps identify the state of the data used in this study, in

388   terms of scale updates/ corrections etc., which is important information because the same

389   datasets may be found in other data-repositories as updated versions with scale changes

390   and /or modifications. As the data preparation is critical to the results, we describe the

391   detailed methods for data preparation used in this study in the following sections.

392

393 ***Data Matching and Reference time Series:*** To match the appropriate co-located and

394 same-flask measurements from the 7 laboratories for comparison, participants agreed to

395 submit measurement results that include information on sample collection time (in

396 Coordinated Universal Time (UTC)), collection method, flask identification, measurement

397 value, quality control flag, and analytical instrument identification. Matching algorithms

398 identify and separate same-flask measurements (samples with identical collection date/time

399 and container ID) from co-located measurements. All data that have been flagged as "valid"

400 by each individual laboratory, are used.

401

402 All same-flask measurements from ALT are differenced from measurements by ECCC, on a

403 one-to-one basis (i.e., laboratory minus ECCC). All co-located flask measurements from

404 ALT, CGO and MLO are differenced from the reference time series of NOAA for CO_2, CH_4,

405 N_2O, and SF_6 and INSTAAR for $\delta^{13}C$ and $\delta^{18}O$ of CO_2 (laboratory minus NOAA or

406 INSTAAR). Ideally, the reference time series should demonstrate consistency over the entire

407 comparison period, have minimal gaps, and accurately represent the true abundance of the

408 atmospheric trace gas constituents at the sites. In practice we do not have a single

409 laboratory who we know to be the truth, so we must choose one that best meets our

410 requirements. NOAA and INSTAAR were chosen because their records span the entire

411 period of our study with minimal data gaps. Also, by hosting the WMO Central Calibration

412 Laboratory for CO_2, CH_4 and N_2O, NOAA is well placed to assess measurements on the

413 WMO scales and INSTAAR, by virtue of their close association, is an appropriate choice for

414 the stable isotopes of CO_2. Further, NOAA/INSTAAR has extensive and well-documented

415 quality control procedures in place to ensure internal consistency of its measurements

416 [**Conway et al., 1994; Dlugokencky et al., 1994; Trolier et al., 1996**].

417

418 ***Co-located Data Pool and Analyses***: Prior to any ALT, CGO and MLO co-located analyses,

419 data pools were created for each site and species, consisting of no more than two valid

420 measurements from each laboratory (including NOAA and INSTAAR) for each day of

421 sampling (sampling episode). Since most participants collect a pair of air samples during

422 each sampling episode, two measurement results are typically available. When more than

423 two valid measurements exist for a given sampling episode from a laboratory, we select two

424 at random from the set of available measurements. For example, three (and sometimes

425 four) MPI-BGC flask air samples are collected during each sampling episode at Alert, so two

426 measurements are selected at random from the available valid MPI-BGC measurements and

427 added to the data pool. If there is only one valid measurement available from one of the

12

428   laboratories, we do include that single sample in the data pool. This data pool process

429   allows for a more equal representation for all laboratories. The first analysis performed using

430   the ALT data pool, was the calculation of mean flask pair differences for CO_2, $\delta^{13}C$-CO_2,

431     $\delta^{18}O$-CO_2, CH_4, N_2O and SF_6 for each participating laboratory and these can be found in

432   **Tables S3** to **S8**. These flask pair differences could be used as a proxy of individual lab

433   uncertainties. The discussion of these differences will be found in future sections.

434

435   For all sites, each laboratory's individual data points in the pool are differenced from the

436   reference time series data in the same pool (i.e. NOAA or INSTAAR). In most cases, the

437   reference time series has two data points, which are averaged and that value is then

438   differenced from each point of the other laboratory. If the reference time series has only one

439   data point for a certain sampling episode, that single point is used for each point of the other

440   laboratory. Our co-located comparison strategy produces a set of difference time series

441   (laboratory minus reference) for each individual trace gas species and isotope measurement

442   record. Before analyzing the time series, we first examined characteristics of their

443   distributions and found that, in general, they are not normally distributed (non-parametric).

444   The statistical approach carried out in this study is based on the assumption of non-normal

445   distributions. It is quite common to observe a pattern of systematic differences (bias) that

446   can be persistent for many months and then change either abruptly or gradually into a

447   different pattern. Thus, we summarize each distribution of individual differences using

448   annual median values with an estimate of the 95% confidence interval (CI), which makes no

449   assumptions about the distribution of the "true" difference population. The 95% CI is

450   computed using methods described by [**Campbell et al., 1988**]. In this way, our initial

451   statistics should not be unduly influenced by outliers. The final derived annual median

452   deviations are compared to the target goals outlined by the WMO GAW greenhouse gas

453   program to assess the level of agreements of individual datasets with the reference

454   laboratory.

455

456   **2.6 Level of Agreement between Multiple Measurement Records**

457

458   In addition to the assessment of individual laboratory co-located comparisons, we attempt to

459   estimate the overall level of grouped agreement from multiple measurement records for each

460   species using two approaches. The first approach provides the 95th percentiles of the

461   individual differences of all laboratory's measurements relative to NOAA's or INSTAAR's

462 corresponding observation. However, because variations in NOAA's or INSTAAR's

463 observational records might impact the results, we also report a second proxy for the level of

464 grouped agreement, i.e., two standard deviations (2-sigma) from the means of each weekly

465 sampling episode, which would define a region that includes 95 percent of all the

466 measurement values. Although less susceptible to bias by NOAA or INSTAAR, this grouped

467 proxy is also not ideal because the introduction of new programs could potentially alter the

468 mean and hence the 2-sigma of the group. In addition, the use of 2-sigma values is less

469 reliable than using percentiles for skewed distributions. But by providing both measures for

470 the level of agreement, we hope that any limitation of one measure over the other can be

471 compensated when interpreting them together. The values determined by both methods

472 reflect the overall maximum bias between the measurement records from multiple monitoring

473 programs.

474

475 **2.7 Data Visualization**

476

477 For each trace gas and isotope comparison, we have prepared one figure (Figures 1-6),

478 consisting of several graphs each. For CO_2, $\delta^{13}C$-CO_2, $\delta^{18}O$-CO_2, CH_4 and N_2O, the figures

479 include five graphs each, from (a) to (e), but for SF_6 there are only four graphs labeled (a) to

480 (d). These figures, along with three data summary tables, are designed to facilitate

481 visualizing and interpreting our results. Graph (a) in these figures displays the time series of

482 each laboratory's measurements. It highlights the long-term trend, seasonal patterns, and

483 natural variability in the records and provides context for the comparison results. Graph (b)

484 consists of several panels, each showing the individual co-located measurement difference

485 (laboratory minus reference) for each laboratory. Differences exceeding the graph's y-axis

486 range are plotted with an "X" symbol; however, these data points are still included in all

487 analysis procedures. The dark shaded band, which is also shown in graphs (c) – (e),

488 represents the WMO/GAW recommended target of measurement agreement for well-mixed

489 air at remote sites in the Northern Hemisphere. Results from past WMO/IAEA Round Robin

490 experiments [Global Monitoring Laboratory - Carbon Cycle Greenhouse Gases (noaa.gov)]

491 are plotted as differences (laboratory minus NOAA or INSTAAR) with yellow triangles,

492 representing each laboratory's level of consistency with the reference lab on scale at the time

493 of the experiment. **Table S1** shows Round Robin differences versus NOAA or INSTAAR for

494 all laboratories over the time period (only RR data that are on the same scale as data in the

495 paper have been included). Graph (c) shows, for each laboratory, the annual medians of the

496 differences plotted in graphs (b) with the lower and upper limits of estimated 95% confidence

497   intervals (CI). The fourth graph, Graph (d), for all species except SF_6, shows the same

498   analysis as that done at Alert in graphs (c) but for the co-located comparison experiments

499   between SIO, CSIRO and NOAA at MLO and between CSIRO and NOAA at CGO. Graph

500   (d) for SF6 is the same as Graph (e) for the others, which shows the individual co-located

501   measurement difference (laboratory minus reference) for all the laboratories as a collective.

502   The blue line shows annual values of 95th percentile ranges (2.5 and 97.5), and the pink line

503   shows annual means of 2-sigma for the weekly sampling episodes. For comparison

504   purposes, we have included the annual means, shown in yellow, of the 2-sigma for the

505   combined weekly sampling episodes between CSIRO, SIO, and NOAA at MLO.

506

507   In addition to the main figures and tables, supplementary figures and tables are included for

508   some species when applicable.

509

510   **3. Results and Discussion**

511

512   As we consider results from 17 years of comparison experiments at Alert, a practical

513   indicator of success is if the measurement agreement reported here falls within the

514   WMO/GAW recommended target levels for network consistency based on well-mixed

515   background air records (**GAW Report #255)**. In other words, it could be assumed that using

516   these records together would not introduce significant uncertainties, if the agreement

517   between independent Alert atmospheric records is consistently within the WMO/GAW

518   measurement agreement goal over the study period.

519

520   In this work, we assess the level of agreement for those individual measurement records at

521   Alert by evaluating the differences related to the reference time series and evaluate these

522   differences as annual and overall median values. When persistent differences exceed the

523   WMO/GAW recommended targets, we then consider results from same-flask and same-

524   cylinder experiments to confirm the differences if data is available. To support the results at

525   Alert, the corresponding comparisons at MLO and at CGO are also evaluated.

526

527   We recognize that for some species, the network comparison goals may not be currently

528   achievable within current measurement and/or scale transfer uncertainties and that these

529   goals are targeted for application areas which require the smallest possible bias among

530   different datasets for the detection of small trends and gradients. However, there are, of

531   course, other application areas where such tight comparison goals may not be required, such

532   as in urban emission estimates, long-term trend analysis, as well as in some regional

533   modelling studies where uncertainties in air transport, for example, overshadow

534   measurement uncertainties. Our work in this study could provide more confidence on the

535   uncertainty estimation for these applications as well.

536

537   **3.1 CO_2**

538

539   All measurements are reported in this paper relative to the WMO X2007 CO_2 mole fraction

540   scale [**Zhao and Tans, 2006**], except for those from SIO, which are reported on the SIO

541   X08A scale [**Keeling et al., 2016**]. This data analysis was completed prior to the latest scale

542   upgrades by NOAA (as the WMO Central Calibration Laboratory) to the WMO X2019 scale

543   and by SIO to the SIOX12A scale. Future comparisons within the WMO community should

544   evaluate the implementation of these new scales. Measurements of atmospheric GHGs are

545   reported in units of dry air mole fraction. CO_2 is reported as micromoles CO_2 per mole of dry

546   air ($\mu mol\ mol^{-1}$), abbreviated ppm.

547

548   As noted above, **Figure 1 (a)** shows the individual co-located atmospheric CO_2

549   measurement records from air samples collected at Alert (1999-2016). For reference, the

550   average flask pair difference and 1-sigma (standard deviation) for each individual laboratory

551   can be found in **Table S3**. **Figure 1 (b)** shows individual co-located measurement

552   differences (laboratory minus NOAA) along with the darkly-shaded WMO recommended

553   target level of ±0.1 ppm CO_2. Results from the WMO/IAEA Round Robin experiments

554   spanning this period are indicated by yellow triangles. The annual median values with 95%

555   CI for each laboratory's difference distribution are shown in **Figure 1 (c)**. A summary of

556   these results is listed in **Table S9**.

557

558   The overall (1999-2016) median difference of all available individual measurements from

559   each laboratory relative to NOAA (**Table S9**) suggests that the CSIRO, MPI-BGC, SIO,

560   UHEI-IUP and ECCC CO_2 records from Alert are consistent with the NOAA record to close to

561   the WMO recommended ±0.1 ppm CO_2 window at the 95% CI. However, it is important to

562   be aware that at higher temporal resolution, e.g. yearly, we often observe median differences

563   that exceed the WMO target for one or more consecutive years. As an example, ECCC has

564   a persistent bias of approximately -0.14 ppm from 2001-2007, which is then reduced in 2008.

565   UHEI-IUP meets the WMO recommended target window from 2005-2008, but has a bias of

566   approximately -0.13 ppm from 2009-2016; the reason for these differences are unclear. An

567   instrument change by SIO in 2012, from an NDIR to a CRDS analyzer, can be seen as a

568   slight reduction of noise in the difference data (Figure.1(b)), and the results seem to be

569   slightly more positive after the change, but the results are still within the WMO target.

570   Measurement differences between LSCE and NOAA show that LSCE is consistently high

571   relative to NOAA, resulting in annual differences that exceed the WMO target. However, if

572   we exclude results from the first two comparison years, the LSCE median value offset

573   appears stable at approximately +0.11 ppm CO_2. These findings are consistent with annual

574   median results from the same-flask comparison at Alert, where LSCE measurements tend to

575   be greater than ECCC measurements of the same-flask sample (**Figure S1** and **Table S10**).

576   The overlaid WMO Round Robin results (**Figure 1(b), Table S1**) show reasonable

577   consistency between the LSCE internal scale and the WMO CO_2 mole fraction scale.

578

579   **Figure S2** shows median differences (laboratory minus NOAA) by month for each laboratory

580   using data from the entire 17-year period. Overall, with the exception of SIO, we found no

581   obvious evidence of significant seasonal bias in the co-located CO_2 difference distributions.

582   The SIO measurements relative to NOAA during the May-September period relative to the

583   October-March period possibly showed a bias on the order of 0.25 ppm. A similar monthly

584   analysis (not shown here) using results from the SIO and NOAA co-located comparison

585   experiment at Mauna Loa (MLO) did not show a similar seasonal bias result, suggesting that

586   the observed seasonal bias between SIO and NOAA at Alert may be unique to this site. The

587   reason for this is unclear; the sampling at both sites is very similar.

588

589   **Figure 1(d)** provides the results from similar co-located comparison experiments between

590   CSIRO, SIO and NOAA at MLO, and at CGO, which are plotted with the results from Alert.

591   **Table S11** shows that the overall median difference of all individual measurements of CSIRO

592   relative to NOAA is -0.07 (95% CI: -0.09, -0.04 ppm) at MLO and 0.03 (95% CI: 0.02, 0.03

593   ppm) at CGO, respectively, which are relatively consistent with our findings at Alert of -0.05

594   (95% CI: - 0.06, -0.03) ppm. Also included in the figure are results from co-located

595   comparison experiments between SIO and NOAA at MLO where the overall median

596   difference is -0.11 (95% CI: -0.13, -0.10) ppm CO_2. This difference is larger than our findings

597   at Alert of -0.02 (95% CI: -0.04, -0.01) ppm, but is still close to the target window of ±0.1

598   ppm.

599

600   **Figure 1(e)** shows individual co-located CO_2 measurement differences, in ppm, relative to

601   NOAA for all the laboratories as a collective. Differences exceeding the y-axis range are

602 plotted with an "X" symbol on the appropriate extreme axis. For the approach of using the

603 2.5 and 97.5 percentiles of the aggregated differenced data (laboratory minus NOAA), an

604 overall collective agreement level of -0.51 to +0.53 ppm (N=5691) was found for the seven

605 laboratories. The corresponding data can be found in **Table S12**. For the approach of using

606 annual means of the 2-sigma variation of weekly sampling episodes, an overall

607 measurement agreement is within the ± 0.37 ppm window (N=923) also at 95% of CI. For

608 comparison purposes, we have included the annual means of the combined 2-sigma

609 variation results at MLO (**Fig. 1(e)** and **Table S12**) shown as the yellow lines (no individual

610 data points are shown) with a comparable result of ± 0.34 ppm (N=905).

611

612 The observed measurement differences (as annual medians) found in this study can also

613 provide a first estimate of time-dependent uncertainties of observations from a single

614 laboratory. To assess the impacts of those uncertainties on related applications (e.g., long-

615 term trend analysis), we estimate long-term trends of CO_2 from the six individual datasets

616 (CSIRO, MPI-BGC, UHEI-IUP, SIO, ECCC, NOAA) for various 11 and 12-year time periods

617 (2005-2016, 2005-2015, 2006-2016) via Nakazawa's curve-fitting routine (Nakazawa et al.,

618 1997). **Table S13** shows very consistent results for these applications. The long-term

619 increases in CO_2 concentrations are 23.62 (2.15 ppm/year) ± 0.40 ppm (2-sigma) for 2005-

620 2016, 21.11 ± 0.38 ppm (2-sigma) for 2005-2015, and 20.87 ± 0.22 ppm (2-sigma) for 2006-

621 2016, respectively. The relative differences between the independent datasets are within a

622 narrow range of 1.5 - 2.4 %, indicating that reliable results can be achieved from these

623 individual datasets for long-term trend analysis (>10 years). It is likely that much larger

624 relative uncertainties would be involved in annual growth rate determination using the

625 corresponding datasets.

626

627 **3.2 $\delta^{13}C$ of CO_2**

628

629 Stable carbon isotopic ratio measurements in CO_2 are reported commonly as delta values

630 [**McKinney et al., 1950; Craig, 1957; Faure, 1986; O'Neil, 1986; Gonfiantini, et al., 1993;**

631 **Coplen, 1994; Hofes, 1996; Trolier et al., 1996**]. A delta value defined here is the relative

632 deviation of two isotopic ratios between a sample and the standard, i.e., the primary VPDB-

633 CO_2 or VPDB scale (VPDB: Vienna Pee Dee Belemnite). As the numerical value of a

634 relative deviation is usually very small (close to 10^{-3}), it is normally multiplied by 10^3 and

635 expressed in permil (‰) as in the following relationship [**Coplen, 1994; Coplen et al., 2002**]:

636 $$\delta^{13}C_{samp/VPDB-CO2} = [((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{VPDB-CO2})-1] \times 10^3 ‰$$

637   There is no single approach to the realization of the VPDB scale amongst individual

638   laboratories (**Table 5**); in other words, although the laboratories have created local scales

639   relative to VPDB through a link to NBS19, small inaccuracies in establishing this link may

640   introduce scale differences between the measurement records. This should be kept in mind

641   while interpreting the differences between the data records.

642

643   **Figure 2(a)** shows the individual co-located atmospheric $\delta^{13}C$-CO_2 measurement records at

644   Alert (1999-2016) and **Figure 2(b)** shows individual co-located measurement differences

645   (laboratory minus INSTAAR) by laboratories. The average overall flask pair difference and

646   1-sigma standard deviation for each individual laboratory can be found in **Table S4**. The

647   overall median difference results (**Figure 2(c), Table S14**) seem to show that ECCC's $\delta^{13}C$-

648   CO_2 records from Alert agree with INSTAAR to within ±0.01‰ at the 95% CI, although the

649   comparison period was relatively short (1999-2009) and the results change in both

650   directions. Similar to the CO_2 results discussed previously, it is again important to be aware

651   that at higher time resolution, we observe periods where the differences significantly exceed

652   the WMO target and show changes in sign that persist for one or more consecutive years.

653   For SIO, we observe a persistent positive offset between SIO and INSTAAR measurements

654   with a median of 0.03 (95% CI: 0.02, 0.03) ‰, which exists for much of the comparison

655   period. We also observe that while the overall median differences for CSIRO, MPI-BGC, and

656   UHEI-IUP relative to INSTAAR exceed the WMO target window with persistent negative

657   biases ranging from -0.02 to -0.03 (95% CI: -0.04, -0.02) ‰, the results suggest that the Alert

658    $\delta^{13}C$-CO_2 records from these 3 laboratories show more agreement with each other than with

659   the INSTAAR reference. It is noted that INSTAAR's measurements are linked to the VPDB-

660   CO_2 scale through the calibrations performed by MPI-BGC (the WMO Central Calibration

661   Laboratory: CCL) via the JRAS-06 realization. The agreement between INSTAAR and MPI-

662   BGC appears to be better after 2015, however, prior to 2015, a bias seems to persist (**Figure

663   2(c)**). As more laboratories within the community move towards linking their isotopic

664   measurements of air CO_2 to the VPDB-CO_2 scale through the JRAS-06 realization and more

665   comparison results are ultimately expanded over longer time periods and at larger spatial

666   scales, this may improve our ability to assess some of the issues we are currently

667   experiencing. All LSCE annual median values exceed the target window and show that

668   LSCE co-located measurements are consistently more negative relative to INSTAAR with an

669   overall median difference of -0.15 (95% CI: -0.16, -0.14) ‰ over the available period (2007-

670   2013). LSCE is aware of ongoing issues with the traceability of their laboratory scale, which

671   likely accounts for the observed results. Thus, we exclude LSCE measurements from our

672 estimate of the grouped measurement agreement (discussed later). It is also noticed that

673 based on T- test results (not shown), the calculated mean differences between laboratories

674 and INSTAAR are statistically significant for almost all of the labs, although they are small;

675 these results indicate that systematic differences do exist, which likely include scale

676 realization differences.

677

678 Analysis of the median differences by month for each laboratory relative to INSTAAR (not

679 shown) over the available periods suggests there are no significant seasonal dependencies.

680 We also note that corresponding results from available Round Robin experiments (**Figure

681 2(b), Table S1**) seem generally similar to the individual flask measurement differences from

682 INSTAAR, which provides evidence that analytical procedure, calibration methods and the

683 approach for realization of the VPDB scale utilized by the participating laboratories may play

684 an important role in the results.

685

686 **Figure 2(d)** and **Table S15** show the similar co-located comparison experiments for δ^{13}C-

687 CO_2 between CSIRO, SIO and INSTAAR at Mauna Loa (MLO) and between CSIRO and

688 INSTAAR at Cape Grim (CGO). These results are also plotted with the results from Alert.

689 The overall median difference of all individual measurements for δ^{13}C-CO_2 (CSIRO minus

690 INSTAAR) is -0.02 (95% CI: -0.02, -0.01) ‰ at MLO and -0.01 (95% CI: -0.01, -0.01) ‰ at

691 CGO, respectively, which are fairly consistent with the findings at Alert of -0.03 (95% CI: -

692 0.03, -0.02) ‰. The corresponding median difference value of SIO from INSTAAR at MLO is

693 0.02 (95% CL: 0.02, 0.02) which is also close to the values of 0.03 (95% CL: 0.02, 0.03) at

694 Alert.

695

696 For an estimation of the overall grouped measurement agreement among the six

697 independent δ^{13}C-CO_2 records at Alert (LSCE has been excluded), the results from two

698 approaches are included in **Figure 2(e).** The estimated overall measurement agreement

699 (**Table S16**) among the six independent Alert δ^{13}C-CO_2 records is within the -0.09 to +0.07

700 ‰ window (n=3256). The pink lines in **Figure 2(e)** represent the annual means of 2-sigma of

701 each weekly δ^{13}C-CO_2 sampling episode. The estimated overall measurement agreement

702 among the six independent Alert δ^{13}C-CO_2 records is within the range of ± 0.06 ‰ (n=899).

703 For comparison purposes, the annual means of the 2-sigma values from MLO in **Figure 2(e)**

704 (yellow lines) and **Table S16**, show comparable results of ± 0.05 ‰ (n=756).

705

706 **3.3 δ^{18}O of CO_2**

707

Oxygen isotopic ratio measurements in CO_2 are also commonly reported as delta values. A

delta value is defined as the relative deviation of two isotopic ratios between a sample and

the standard (i.e., the primary VPDB-CO_2 scale). Similar to $\delta^{13}C$, the numerical value of the

relative deviation in $\delta^{18}O$ is usually very small and is normally multiplied by 10^3 and

expressed in permil (‰), as in the following relationship:

$$\delta^{18}O_{samp/VPDB\text{-}CO2} = [((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VPDB\text{-}CO2})\text{-}1] \times 10^3 \text{ ‰}$$

The "-CO_2" after VPDB indicates that the scale is linked via the CO_2 from the VPDB

carbonate material by a standard procedure of acid digestion using phosphoric acid at 25

degrees Celcius [**McCrea, 1950; O'Neil, 1986; Brand et al., 2009; Wendeberg et al, 2011;**

Huang et al., 2013]. If the local scale used by different laboratories does not follow the

same procedure, then $\delta^{18}O$-CO_2 results may not be compatible.

719

Figure 3(a) shows the individual co-located atmospheric $\delta^{18}O$-CO_2 measurement records at

Alert (1999-2016) and **Figure 3(b)** shows individual co-located measurement differences

(laboratory minus INSTAAR) along with the recommended WMO target level of

measurement agreement. For reference, the average flask pair difference and 1-sigma

variability for each individual laboratory can be found in **Table S5.** The overall (1999-2016)

median differences of all available individual measurements from each laboratory relative to

INSTAAR (**Figure 3(c)**, **Table S17)** show that the $\delta^{18}O$-CO_2 records by MPI-BGC and ECCC

are each roughly compatible with the INSTAAR record to within the WMO recommended

±0.05‰ target window, and SIO and CSIRO are just slightly higher than the target at the 95

% CI (by 0.01‰ and 0.03 ‰, respectively). Similar to CO_2 and $\delta^{13}C$, larger systematic

differences are observed in higher temporal-resolution windows and annual median values

often exceed the WMO target in opposite directions. For example, for CSIRO's median

differences from 1999-2009, the majority of the values fall within the target window.

However, a positive bias of approximately 0.16 ‰ becomes noticeable from 2010 onwards.

LSCE measurements tend to be more negative relative to INSTAAR with an overall median

value of -0.12 (95% CI: -0.15, -0.07) ‰ and UHEI-IUP measurements tend to be more

positive relative to INSTAAR, with an overall value of 0.23 (95% CI: 0.20, 0.27) ‰.

737

However, the overlaid available results from the periodic Round Robin experiments (**Figure**

3(b) Table S1) show less differences than those in flask samples between INSTAAR and the

individual laboratories, including CSIRO, MPI-BGC, UHEI-IUP and ECCC; this infers that the

larger differences observed in flask measurements might be due to variable moisture levels

742 in the samples. Analysis of annual median differences by month for each laboratory relative

743 to INSTAAR (not shown) does not suggest any seasonal dependencies.

744

745 **Figure 3(d)** and **Table S18**, respectively, show the results of $\delta^{18}O$-CO_2 from similar co-

746 located comparison experiments between CSIRO and INSTAAR at Mauna Loa (MLO) and at

747 Cape Grim (CGO), plotted with the results from Alert. The overall median difference of all

748 individual measurements for CSIRO relative to INSTAAR is 0.18 (95% CI: 0.17, 0.19) ‰ at

749 MLO and 0.21 (95% CI: 0.21, 0.22) ‰ at CGO, respectively. While the MLO and CGO

750 results are more or less consistent with each other, they do not align with our overall findings

751 at Alert, which show a value of 0.08 (95% CI: 0.06, 0.10) ‰. However, as mentioned before,

752 CSIRO's median at ALT from 2010 onwards (0.16 ‰) is fairly similar to the overall value at

753 MLO from 1999 to 2016. Further data may be needed to make any comments on

754 measurement consistency across entire networks for CSIRO and NOAA for $\delta^{18}O$-CO_2. The

755 results between SIO and INSTAAR at Alert and at MLO show a consistent pattern in the

756 difference distribution (SIO relative to INSTAAR) at both sites, with the overall median

757 difference at MLO being 0.03 (95% CI: 0.02, 0.04) ‰ and the median difference at Alert

758 being 0.06 (95% CI: 0.05, 0.08) ‰ and thus, it is likely that the comparison results at first

759 estimation, are representative of measurement consistency across entire networks for SIO

760 and INSTAAR.

761

762 Finally, we estimate a grouped measurement agreement among the seven independent Alert

763 $\delta^{18}O$-CO_2 records by aggregating all individual differences from participating laboratories

764 (relative to INSTAAR) to compute the 2.5 and 97.5 percentiles. This upper and lower limit

765 contains 95% of the entire difference distribution from all laboratories and represents our

766 best estimate of measurement agreement (blue lines in **Figure 3(e)**). **Table S19** shows that

767 the 7 independent co-located $\delta^{18}O$-CO_2 records at Alert are compatible to within a -0.50 to

768 +0.58 ‰ window (N= 2738). For the approach of using the means of the 2-sigma variation

769 from weekly sampling events through the entire period, the corresponding overall

770 measurement agreement is within the range of ± 0.31 ‰ (n=872; pink lines in **Figure 3(e)**).

771 For comparison purposes the annual means of the 2-sigma values from MLO in **Figure 3(e)**

772 (yellow lines) and **Table S19**, show a smaller range of ± 0.19 (n=729) ‰.

773

774 **3.4 CH$_4$**

775

776 All CH$_4$ measurements are reported relative to the WMO X2004A CH$_4$ mole fraction scale,

777 which is described by **Dlugokencky et al. [2005]** with updated information (2015) available

778 at https://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html (last access: 08/17/2022).

779 Measurements of atmospheric CH$_4$ are reported in nanomoles (billionths of a mole CH$_4$) per

780 mole of dry air and abbreviated ppb (parts per billion).

781

782 **Figure 4(a)** shows the individual co-located atmospheric CH$_4$ measurement records at Alert

783 (1999-2016) and **Figure 4(b)** shows individual co-located measurement differences

784 (laboratory minus NOAA) along with the recommended target level of measurement

785 agreement and Round Robin results. **Figure 4(c)** shows the annual median values with 95%

786 CI for each laboratory's difference distribution. The WMO/GAW recommended target range

787 is again represented by the dark grey band. **Table S20** summarizes these results.

788

789 The overall (1999-2016) median difference of all available individual measurements relative

790 to NOAA (**Table S20**) suggests that the CH$_4$ records of CSIRO, MPI-BGC, UHEI-IUP, and

791 ECCC from Alert agree with NOAA within the WMO recommended ±2 ppb CH$_4$ compatibility

792 target window. At higher resolution we sometimes observe differences that exceed the

793 target window for one or more consecutive years, without known causes. For example,

794 annual median differences between ECCC and NOAA generally show a consistent offset of

795 approximately -1 ppb except 2003-2004 and 2007, where the offset lies slightly outside the

796 target window. Similar results are observed between LSCE and NOAA where there is a

797 consistent positive offset of ~2 ppb except for 2008 and 2009, where the offset of ~4 ppb lies

798 outside the target window. MPI-BGC and UHEI-IUP show fairly consistent agreement versus

799 NOAA throughout the time period, with just one year outside the target window for MPI-BGC

800 in 2012. Annual differences for CSIRO show a slightly negative bias from 1999-2008 with

801 one year outside of the target window, and a more positive bias from 2009-2016.

802

803 Results from the periodic Round Robin experiments (**Figure 4(b), Table S1**) are consistent

804 with the co-located comparison results for each individual participating laboratory. Analysis

805 of annual median differences by month for each laboratory relative to NOAA (not shown)

806 does not suggest any seasonal dependencies.

807

808 Results from similar co-located comparison experiments between CSIRO and NOAA at

809 Mauna Loa (MLO) and at Cape Grim, (CGO) are plotted with the results from Alert in

810 **Figure4(d)**. As shown in **Table S21**, the median difference of all individual CH$_4$

811   measurements from CSIRO relative to NOAA is 0.66 (95% CI: 0.38, 0.88) ppb for MLO, 0.11

812   (95% CI: -0.07, 0.32) ppb for CGO, and 0.01 (95% CI: -0.19, 0.21) ppb for Alert, respectively.

813   The results are all within the WMO recommended compatibility target window. Therefore,

814   the comparison results at the shared site such as Alert could be representative of

815   measurement consistency across entire networks for CSIRO and NOAA for CH_4.

816

817   Finally, we estimate an overall measurement agreement among the six independent Alert

818   CH_4 records of -4.86 to +6.16 ppb (N=4472) over the entire period of 1999-2016 (**Table S22**),

819   shown in blue lines in **Figure 4(e)**. For the approach of using the means of the 2-sigma

820   variation from weekly sampling events through the entire period, the estimated overall

821   measurement agreement among the six independent Alert CH_4 records is within the range of

822   ± 3.62 ppb (n=887) (pink lines in **Figure 4(e)**). For comparison, we have included the annual

823   means of the combined 2-sigma variation results of ±4.88 ppb (n=375) at MLO in yellow lines

824   (**Figure 4(e)** and **Table S22**).

825

826   **3.5 N_2O**

827

828   All N_2O measurements are reported relative to the NOAA 2006A N_2O mole fraction scale

829   which is described by **Hall et al. [2007]** with updated information (2011) available at

830   https://gml.noaa.gov/ccl/n2o_scale.html. Measurements of atmospheric N_2O are reported as

831   a dry air mole fraction in nanomoles (billionths of a mole N_2O) per mole of dry air and

832   abbreviated ppb (parts per billion). All N_2O measurements in this study were determined

833   using GC-ECD analytical methodology. These systems typically achieved repeatability of

834   0.15 to 0.3 ppb, making the comparisons much noisier and therefore, more difficult to

835   evaluate whether the WMO target goal of ±0.1 ppb has been achieved. Fortunately, several

836   new spectroscopic methods are now available and capable of providing analytical

837   repeatability of 0.04 to 0.1 ppb [**O'Keefe et al., 1999; Griffith et al., 2012**;]. These new

838   methods have a potential to make comparisons less noisy and possibly easier to interpret.

839

840   **Figures 5 (a)-(e)** and **Tables S23-S26** provide the corresponding information for N_2O. The

841   seasonal cycle is more clearly defined in the UHEI-IUP data set (**Figure 5(a)**) than in the

842   other data records due to better precision on their specific GC-ECD. Analytical precision of

843   atmospheric N_2O measurement is estimated using agreement between measurements of air

844   collected in two flasks sampled on the same apparatus at the same time. **Table S7**

845   summarizes average flask pair agreement based on air samples collected at Alert. Using

846 pair agreement to estimate short-term noise, we find UHEI-IUP and NOAA N_2O

847 measurements of flask air with repeatability of 0.13 ± 0.08 ppb and 0.30 ± 0.26 ppb,

848 respectively. The NOAA measurement is less precise because it is derived from a single

849 aliquot of air whereas all other laboratories typically use an average of 2-4 aliquots of sample

850 air. Both NOAA and INSTAAR are limited in the volume of sample that can be used for each

851 of their analyses because of the very large suite of trace gas species measured from the

852 NOAA flask air sample. This has a much more profound impact on estimated N_2O precision

853 than for other trace gas species and isotopes.

854

855 The overall (1999-2016) median difference of all available individual measurements from

856 each laboratory relative to NOAA (**Table S23**) shows that the UHEI-IUP and ECCC N_2O

857 records from Alert are roughly compatible with the NOAA record to within the WMO

858 recommended ±0.1 ppb target window. However, as mentioned in each previous section, at

859 higher resolution, we can observe median differences that well exceed the WMO target for

860 many years. MPI-BGC differences show a consistently positive bias spanning from 2005 to

861 2014, which is reduced by approximately 2-fold in 2015-2016 when they switched from a Mg

862 $(ClO_4)_2$ dryer to a cryocooler. MPI-BGC suggests that these impacts were mostly

863 pronounced during the wetter summer months and attributes the issues to a change in the

864 supplier of the Mg $(ClO_4)_2$. A similar problem was reported by **[Steele et al., 2007]**. There

865 was no evidence of bias for any of the other trace species. Differences between LSCE and

866 NOAA, which initially exceed the target by 1.2 ppb, steadily improve each year. By 2013, the

867 final year of the comparison for LSCE, the annual median difference has improved by a

868 factor of ~10, to 0.15 ppb but still falls outside the WMO target window. Because the results

869 from the same-flask comparison experiment between LSCE and ECCC (**Figure S3**) show a

870 similar difference pattern, this suggests that the sample collection process is not likely the

871 cause of the observed co-located measurement differences. On the other hand, the

872 same-flask air comparison results **(Figure S3, Table S24)** for the other laboratories show

873 that the median differences were mostly able to meet the target window, in contrast to the co-

874 located comparisons, suggesting that there may be factors that are specific to the collection

875 of the air itself causing some of the inconsistency among the various laboratories.

876

877 Results from the periodic Round Robin experiments (**Figure 5(b), Table S1**) are consistent

878 with the co-located comparison results for each participating laboratory. With regard to

879 seasonal dependencies, an analysis of median differences by month (not shown) displayed

consistent offsets for each month indicating that the date of sample collection had no bearing on the annual results.

Earlier, we mentioned that analytical precision (estimated from flask pair agreement) of NOAA measurements is about a factor of 2 worse than UHEI-IUP measurements (**see Table S7**). To explore the impact this may have on our findings, we computed differences relative to the more precise UHEI-IUP N_2O record (**Figure S4**). As expected, we find the uncertainty in annual median differences relative to the more precise UHEI-IUP N_2O record to be considerably smaller than when referenced to NOAA measurements. While the agreement between MPI-BGC and UHEI-IUP measurements improves and the differences of CSIRO and ECCC relative to UHEI-IUP remain more stable over time, our overall findings do not change.

The results from the co-located comparison experiments between CSIRO and NOAA at Mauna Loa (MLO) and at Cape Grim (CGO) (**Figure 5(d), Table S25)** show the median difference of all individual N_2O measurements to be -0.17 (95% CI: -0.21, -0.13) ppb at MLO which is consistent with our findings in Alert of -0.17 (95% CI: -0.20, -0.13) ppb. At CGO this median difference is -0.03 (95% CI: -0.06, 0.00) ppb, which is slightly smaller than the ALT and MLO results. Considering the previously mentioned effects of water on the N_2O measurements, the differences could potentially arise from site-specific sampling parameters, such as CSIRO's change to a cryocooler in 2014 at CGO or NOAA's use of a partially dried sample at CGO (although not at MLO or ALT). However, pinpointing the exact cause is beyond the scope of this paper.

Finally, we estimate a measurement agreement for the six independent Alert N_2O data records as a collective, to be within -0.75 to +1.20 ppb (N= 3957) over the entire period of 1999-2016 (**Table S26**). For the approach of using the means of the 2-sigma variation from weekly sampling events we estimate a corresponding overall measurement agreement of ± 0.64 ppb (n=801) (pink lines in **Figure 5(e)**). For comparison, we have included the annual means of the combined 2-sigma variation results of ± 0.64 ppb (n=366) at MLO in yellow lines (**Figure 5(e)** and **Table S26**).

3.6 SF$_6$

914 All measurements are reported relative to the NOAA X2014 SF_6 mole fraction scale. [**Hall et**
915 **al., 2011; Lim et al., 2017**]. Measurements of atmospheric SF_6 are reported in picomoles
916 (trillionths or 10^{-12} of a mole SF_6) per mole of dry air and abbreviated ppt (parts per trillion).
917 All SF_6 measurements from the 4 laboratories in this study (MPI-BGC, LSCE, ECCC, and
918 NOAA) were determined using GC-ECD analytical methodology. The estimated repeatability
919 of SF_6 measurements, based on replicated injections of standard tank gas, using the dual
920 N_2O/SF_6 GC-ECD system is ~0.04 ppt.
921

922 **Figures 6(a)-(d)** and **Tables S27-S28** show the corresponding information for SF_6. Please
923 note that there is one less figure and table than the other species, because there are no SF_6
924 results from the other sites (MLO and CGO) and the last figure and table have been shifted
925 up by one, compared to other species. **Table S27 and Figure 6(c)** show that the MPI-BGC
926 and NOAA SF_6 measurements meet the WMO recommended ±0.02 ppt SF_6 compatibility
927 window in 11 of the 12 comparison years (2005-2016). Annual median differences between
928 ECCC and NOAA measurements for 2003-2014 show a constant median offset of -0.05 ppt.
929 The annual differences between LSCE and NOAA measurements for 2007 to 2010 show a
930 similar average offset of approximately -0.05 ppt but showed good agreement from 2011 to
931 2013. Results from the periodic Round Robin experiments (**Fig. 6(b), Table S1**) are
932 consistent with the co-located comparison results for each participating laboratory. Again,
933 we find the analysis of median differences by month for each laboratory (not shown) does not
934 indicate any seasonal dependencies.
935

936 We find the 4 independent co-located SF_6 records at Alert (**Table S28**) are consistent to
937 within a window of -0.14 to +0.09 ppt (N=2359) using 2.5 and 97.5 percentiles and ±0.09 ppt
938 (N=723) using the mean of the 2-sigma approach over the time period, respectively. **Figure**
939 **6(d)** shows individual measurement differences relative to the NOAA reference for all
940 laboratories, the WMO recommended target range (dark grey band), and our estimate of the
941 overall measurement agreements (in blue and pink lines). There are no SF6 measurements
942 at MLO or CGO to make general comparisons with the Alert data records.
943

944 **4. Summary and Conclusions**
945

946 We presented a comparison of measurements of CO_2, CH_4, N_2O, SF_6, and the stable isotope
947 ratios of CO_2 ($\delta^{13}C$, $\delta^{18}O$) in co-located air samples collected at Alert, Nunavut, Canada by
948 seven laboratories (ECCC, CSIRO, MPI-BGC, UHEI-IUP, LSCE, SIO, and NOAA (in

949   collaboration with INSTAAR)) spanning 17 years. We also evaluated the consistency of

950   measurements between certain laboratories (CSIRO, SIO & NOAA/INSTAAR) at three sites

951   (ALT, MLO and CGO), where other co-located flask sampling programs operate.

952

953   From this work, we find that the co-located atmospheric CO_2 and CH_4 measurement records

954   from Alert by CSIRO, MPI-BGC, SIO, UHEI-IUP, ECCC, and NOAA are compatible to the

955   WMO network compatibility goals within ±0.1 ppm CO_2 and ±2 ppb CH_4 at the 95% CI,

956   respectively, over the 17-year period. In addition, we find that the co-located comparison

957   programs at MLO and CGO show similar agreement levels to those at Alert within a range of

958   ±0.1 ppm for CO_2 between CSIRO, SIO and NOAA records and within a range of ±2 ppb for

959   CH_4 between CSIRO and NOAA records. An important caveat to these CO_2 and CH_4 results

960   is that we often observe periods where the biases between datasets exceed the WMO target

961   levels and may persist as systematic bias for months or years, which could impact our

962   observed compatibility. Our analysis shows that for δ^{13}C-CO_2, δ^{18}O-CO_2, N_2O and SF_6, our

963   estimate of the overall measurement agreements during the time of this study exceeds the

964   WMO recommended targets. Differences in the respective local scale implementations for

965   the isotopes of CO_2, possible moisture effects for δ^{18}O-CO_2 and the analytical precision of the

966   instruments used for N_2O and SF_6 are possible limiting factors for these results. In addition,

967   the N_2O may have some biases introduced by sample collection procedures.

968

969   Further analysis shows that the overall results observed for CSIRO, SIO and

970   NOAA/INSTAAR's CO_2, CH_4, and δ^{13}C- CO_2 for the study period are roughly consistent

971   among the three sites (ALT, MLO & CGO), implying that merging these records could be

972   done across these specific networks. However, for the δ^{18}O-CO_2 and N_2O records, future

973   data may be needed to make definitive statements about compatibility across networks.

974

975   Although most of the co-located independent CO_2 and CH_4 atmospheric records at Alert

976   meet the WMO recommended targets when considering the results over the entire study

977   period (1999-2016), meeting the compatibility targets for other trace gas species and stable

978   isotopes in CO_2 continues to be a challenge. The independent measurement records could

979   still be used together for various scientific applications (e.g., long-term trend analysis of CO_2

980   in Sect. 3.1), even though individual data points are not fully compatible with the WMO/GAW

981   recommended targets. Furthermore, if we provide data users with the estimated overall

982   measurement agreements for multiple records, they could then take these estimates into

983 account, along with the measurement uncertainties from individual records, while using the

984 data sets for relevant applications.

985

986 For each trace gas species and isotope, we have estimated an overall measurement

987 agreement among the Alert records by aggregating all individual differences from each

988 participating laboratory (relative to the NOAA or INSTAAR reference) and then computing the

989 2.5 and 97.5 percentiles for the entire available periods. This upper and lower limit contains

990 95% of the entire difference distribution from all participating laboratories and represents our

991 best estimate of measurement agreement for these data records. The ranges of the

992 estimated overall measurement agreement when combining all individual flask records from

993 Alert over the entire available periods are -0.51 to +0.53 ppm for CO_2, -0.09 to +0.07 ‰ for

994 $\delta^{13}C$-CO_2, -0.50 to +0.58 ‰ for $\delta^{18}O$-CO_2, -4.86 to +6.16 ppb for CH_4, -0.75 to +1.20 ppb for

995 N_2O, and -0.14 to +0.09 ppt for SF_6, respectively. Using another alternative approach as

996 discussed in Sect. 2.6., we provide the means of the 2-sigma of each weekly sampling

997 episode, involving all participating laboratories over the entire available time period, which

998 are ±0.37 ppm for CO_2, ± 0.06 ‰ for $\delta^{13}C$-CO_2, ±0.31 ‰ for $\delta^{18}O$-CO_2, ± 3.62 ppb for CH_4,

999 ±0.64 ppb for N_2O and ±0.09 ppt for SF6, respectively. Results from this analysis reveal

1000 overall cumulative differences due to errors introduced at one or more steps in the entire

1001 atmospheric measurement process, including sampling and analytical procedures.

1002

1003 In summary, this study assesses the level of measurement agreement among individual

1004 programs by comparing co-located flask air measurements. It enhances confidence in the

1005 uncertainty estimation while using those datasets either individually or collectively across

1006 diverse applications. Conducting such comprehensive analysis regularly is advisable to

1007 detect potential issues and monitor any scale and/or instrumentation changes. It's

1008 recommended that future analyses be carried out every 2 years by a dedicated entity and be

1009 reported regularly during WMO GGMT meetings.

1010

1011 **Data Availability**

1012

1013 All raw data, matched co-located data, supplementary tables, figures and material are

1014 included with this manuscript.

1015

1016 **Author contributions**

1017

1018 DEJW, LH and MKR designed and coordinated the overall flask sampling experiments at
1019 Alert, as well as the comparison effort. Each institute's program lead (DEJW, LH, PBK, RLL,
1020 CEA, AMC, SM, IL, MR[7], AJ, HM, RK) directed their own sampling, analysis and quality
1021 control programs. MKR, AC, RLL, SH, SM, MS, AJ, MR[8], and EJM performed the analysis
1022 for their corresponding institutes. KAM curated and analyzed the data and wrote several
1023 chapters of the initial draft. MKR further curated and analyzed the data. IL, CEA, FV, RK
1024 and SM provided additional input about the contents. MKR, LH and DEJW worked equally
1025 on several revisions and prepared the final manuscript together with FV, as well as reviews
1026 and edits by RLL, PBK, CEA, MM, GP, AMC, SM, IL, SH, AJ, HM, and RK.

1027

1028 **Competing interests**

1029

1030 The authors declare that they have no conflict of interest.

1031

1032 **Acknowledgments**

1033

1044

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1321 **Table 1.** Summary of available observations and flask comparison types for each
1322 participating laboratory during the period of this study at ALT.
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LAB	TYPE OF ICP		1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
ECCC	CO-LOCATED	CO_2, CH_4, N_2O, SF_6	██
		$\delta 13C$, $\delta 18O$	██
	SAME-FLASK	CO_2, CH_4, N_2O, SF_6	█████████████████████████████
		$\delta 13C$, $\delta 18O$ with MPI	████████████
		$\delta 13C$, $\delta 18O$ with CSIRO	███████████████████
CSIRO	CO-LOCATED	CO_2, CH_4, N_2O	██
		$\delta 13C$, $\delta 18O$	██
	SAME-FLASK	CO_2, CH_4, N_2O	██████████████████
		$\delta 13C$, $\delta 18O$	███████████████████
NOAA	CO-LOCATED	CO_2, CH_4, N_2O, SF_6	██
		$\delta 13C$, $\delta 18O$	██
	SAME-FLASK	CO_2, CH_4, N_2O, SF_6	██
SIO	CO-LOCATED	CO_2	██
		$\delta 13C$, $\delta 18O$	██
	SAME-FLASK		
UHEI-IUP	CO-LOCATED	CO_2, CH_4, N_2O	████████████████████████████████████
		$\delta 13C$, $\delta 18O$	████████████████████████████████████
	SAME-FLASK	CO_2, CH_4, N_2O	████████████████████████
MPI-BGC	CO-LOCATED	CO_2, CH_4, N_2O, SF_6	████████████████████████████████████
		$\delta 13C$, $\delta 18O$	████████████████████████████████████
	SAME-FLASK	CO_2, CH_4, N_2O, SF_6	███████████████
		$\delta 13C$, $\delta 18O$	████████████
LSCE	CO-LOCATED	CO_2, CH_4, N_2O, SF_6	██████████████████████████████
		$\delta 13C$, $\delta 18O$	██████████████████████████████
	SAME-FLASK	CO_2, CH_4, N_2O, SF_6	██████████████████████

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1326 **Table 2.1** Summary of flask type, sampling frequency and apparatus used for each
1327 participating laboratory during the period of this study at ALT.

GROUP	FLASK TYPE	SAMPLING FREQUENCY	FILLING APPARATUS	SAMPLE DRYING	INLET HEIGHT
CSIRO	**1999-Nov.2014*** ECCC flasks. **Nov 2014-present** CSIRO 0.5 L pressurized Double valves Teflon (PFA) o-rings ***See section SI for details**	**Variable. See SI for details**	**1999-Aug 2016** SIO sampler **Aug 2016-present** CSIRO/UHEI/ ECCC sampler	cryocooler	10 m Tower
MPI-BGC	**2005-present** 1 L pressurized Double valves PCTFE o-rings	triplet bi-weekly	MPI-BGC sampler	**2005-2015** $Mg(ClO_4)_2$ **2015-present** cryocooler	10 m tower
UHEI-IUP	**2005-present** 1 L pressurized Double valves PCTFE o-rings	1 pair weekly	**2005-Aug 2016** SIO sampler **2016-present** CSIRO/UHEI/ ECCC sampler	cryocooler	10 m tower
LSCE	**2007-2013** 1 L pressurized Double valves PCTFE o-rings	1 pair weekly	LSCE sampler	cryocooler	10 m tower
SIO	**1999-present** 5 L Evacuated Single valve Greased	1 pair weekly	N/A	None	arm's length above head
ECCC	**1999-present** 2 L pressurized Double valves Viton o-rings	1 pair weekly	**1999-Aug 2016** SIO sampler **2016-present** CSIRO/UHEI/ ECCC sampler	cryocooler	10 m tower
NOAA	**1999-present** 2.5 L pressurized Double valves PTFE Teflon o-rings	**1999-2011** 2 pairs weekly **2011-present** 1 pair weekly	Portable sampling unit (PSU)	None	5 m Sample line extending from sampler

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1329 **Table 2.2** Differences of sampling between ALT, MLO and CGO

Group	ALT	MLO	CGO
CSIRO	Different flask types SIO O_2/N_2 sampler Cryocooler,10m,	CSIRO 0.5L flasks Flask pump unit (FPU) $Mg(ClO_4)_2$, 40m,	CSIRO 0.5L flasks FPU (1999-2014),$Mg(ClO_4)_2$; Sherpa unit (2014-2016), cryocooler, 70m,
SIO	Undried, ~2m	Undried, ~2m	N/A
NOAA	Portable sampler unit (PSU), undried, 5m	PSU, undried, 5m; also some flasks from *in situ* air stream, undried, 40m	PSU, partially dried using a condenser, 70m

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1331 **Table 3.** Flask air collection schedule for each participating laboratory at ALT.
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WEEK	INDOOR FLASKS	Typical times (UTC)	INDOOR FLASKS (other)	Typical times (UTC)	OUTDOOR FLASKS	Typical times (UTC)
1	ECCC (1 pair weekly) CSIRO (1 pair as below ***) UHEI-IUP 1 (pair weekly)	14:00-14:30 14:30-15:00 15:00-15:30	MPI-BGC (triplet bi-weekly) LSCE (1 pair weekly)	14:15-14:45 14:45-15:15	NOAA (1 pair weekly) SIO (1 pair weekly)	14:05-14:15 14:05-14:10
2	ECCC 1 (pair weekly) UHEI-IUP (1 pair weekly)	14:00-14:30 14:30-15:00	LSCE (1 pair weekly)	14:15-14:45	NOAA (1 pair weekly) SIO (1 pair weekly)	14:05-14:15 14:05-14:10

1333 *** CSIRO: **biweekly** from Nov. to May; **weekly** rest of the year
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Table 4. Summary of types of instrumentation, repeatability and scales used for the flask air analysis at each participating laboratory during the period of this study.

Laboratory	Species	Duration of instrument use	Instrument type	Calibration Scale
CSIRO	CO_2, CH_4	1999- 2016	GC-FID[1]	X2007, X2004A
	N_2O	1999- 2016	GC-ECD[2]	X2006A
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	1999- 2016	IRMS[3]	Local (see Table 5)
MPI-BGC	CO_2, CH_4, N_2O, SF_6	2005- 2016	GC-FID[4]/ GC-ECD[4]	X2007, X2004A, X2006A, X2014
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	2005- 2016	IRMS[3]	Local JRAS-06 (see Table 5)
UHEI-IUP	CO_2, CH_4, N_2O	2005- 2016	GC-FID[4]/ GC-ECD[4]	X2007, X2004A, X2006A
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	2005- 2016	IRMS[3]	Local (see Table 5)
LSCE	CO_2, CH_4, N_2O, SF_6	2007- 2013	GC-FID[4]/ GC-ECD[4]	X2007, X2004A, X2006A, X2014
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	2007- 2013	IRMS[3]	Local (see Table 5)
SIO	CO_2	1999- 2012	NDIR[5]	X08A
		2012- 2016	CRDS[6]	X08A
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	1999- 2000	IRMS[7]	Local (see Table 5)
		2000-2016	IRMS[8]	Local (see Table 5)
ECCC	CO_2	1999- 2006	NDIR[9]	X2007
	CO_2, CH_4, N_2O, SF_6	1999- 2016	GC-FID[4]/ GC-ECD[4]	X2007, X2004A, X2006A, X2014
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	1999- 2009	IRMS[3]	Local (see Table 5)
NOAA/ INSTAAR	CO_2	1999-2016	NDIR[10]	X2007
	CH_4, N_2O, SF_6	1999- 2016	GC-FID[4]/ GC-ECD[4]	X2004A, X2006A, X2014
	$\delta^{13}C$ and $\delta^{18}O$-CO_2	1999- 2016	IRMS[8]	Local JRAS-06 (see Table 5)
		2005- 2016	IRMS[11]	Local JRAS-06 (see Table 5)

[1] Carle 400 (repeatability of 0.05 ppm for CO_2, 3 ppb for CH_4)
[2] Shimadzu (repeatability of 0.2 ppb for N_2O)
[3] MAT252 (repeatability of 0.02 permil for ^{13}C-CO_2 and 0.04 permil for ^{18}O-CO_2)
[4] Agilent 5890/6890/7890 (repeatability of 0.05 ppm for CO_2, 3 ppb for CH_4, 0.2 ppb for N_2O, and 0.04 ppt for SF_6)
[5] APC model 55 (repeatability of 0.05 ppm for CO_2)
[6] Picarro (repeatability of 0.01 ppm for CO_2)
[7] VGII (repeatability of 0.02 permil for ^{13}C-CO_2 and 0.04 permil for ^{18}O-CO_2)
[8] Micromass Optima DI (repeatability of 0.02 permil for ^{13}C-CO_2 and 0.04 permil for ^{18}O-CO_2)
[9] Siemens Ultrama (repeatability of 0.05 ppm for CO_2)
[10] Licor (repeatability of 0.05 ppm for CO_2)
[11] GV Isoprime DI (repeatability of 0.02 permil for ^{13}C-CO_2 and 0.04 permil for ^{18}O-CO_2)

1358 **Table 5.** Summary of δ^{13}C-CO_2 and δ^{18}O-CO_2 scale propagation and calibration strategies
1359 employed by each participating laboratory.
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	CSIRO	MPI-BGC	UHEI-IUP	SIO	INSTAAR	ECCC
Realization of VPDB-CO_2 scale	local*	Local (JRAS-06)	local	local	JRAS-06	local
Realization approach and frequency	Calibration of pure CO2 was done in 1987, 1994 and 2009 using NBS19 and transferred to a suite of CO_2-in-air standards that are independently maintained. The value assignment is consistent with the MPI-BGC scale for d13c.	Calibration was done at the time of implementation and is maintained by various high pressure air cylinders since then.	About once per year. Transfer to internal pure CO2 gases (Oberlahnstein and Pflanzenstandard) used for daily MSP calibration	A calibration was done in 1994 and maintained CO_2-in-air standards since	Current/recent CO2-in-air standards measured against MPI-BGC standards on JRAS-06. Previous standards tied through "linking standards"	Once per year since 2001 via NBS19, NBS18 & two lab-carbonate standards (Cal1 &2) measured together against the same CO_2 working reference
Primary reference material	NBS19	NBS19	Pure CO_2: RM8562, 8563, 8564	Carbonates: NBS19; Pure CO_2: NBS16,17;	NBS19 via JRAS-06 cylinders	Carbonates: NBS19 &NBS18
^{17}O correction	Brand et al., 2010	Santrock et al., 1985 with IUPAC recommended values for "lambda" and "k" coefficients (Brand et al., 2010).	Santrock et al., 1985 (with coefficients =0.5 and k=0.008335)	Craig 1957	Brand et al., 2010	Craig 1957/ Allison et al., 1995
N_2O correction	Mook and Jongsma (1987) using measured CO2 and N2o amount fractions.	Ghosh et al., 2004	Mook and Jongsma (1987) with measured N_2O	Mook and Jongsma (1987) with estimated N_2O	Mook and Jongsma (1987) with measured N_2O	Mook and Jongsma (1987) with measured N_2O
scale contraction correction	Explicitly monitored, small, and measurements corrected.	Monitored, negligible, no correction applied	Monitored, negligible, no correction applied		Monitored by surveillance cylinders, negligible due to identical treatment, not corrected for	Monitored, negligible, no correction applied
QAQC	Suite of surveillance cylinders. Use of air standards also corrects for uncorrected for variability.		Suite of surveillance cylinders		Suite of surveillance cylinders	Regularly daily monitoring during analysis using the ECCC "Big Delta" method, i.e., the relative difference between the two lab-carbonates

references	Allison and Francey, 2007	Wendeberg et al. 2011 and references therein	Neubert, R., 1998	Guenther et al., 2001;Bollen-bacher et al., 2000; Lueker et al., 2020	Trolier et al., 1996, Michel, S., 2022	Huang et al., 2013

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1362 * A realization of VPDB via an MPI-BGC value-assigned tank and revisions to all CSIRO data is in progress.
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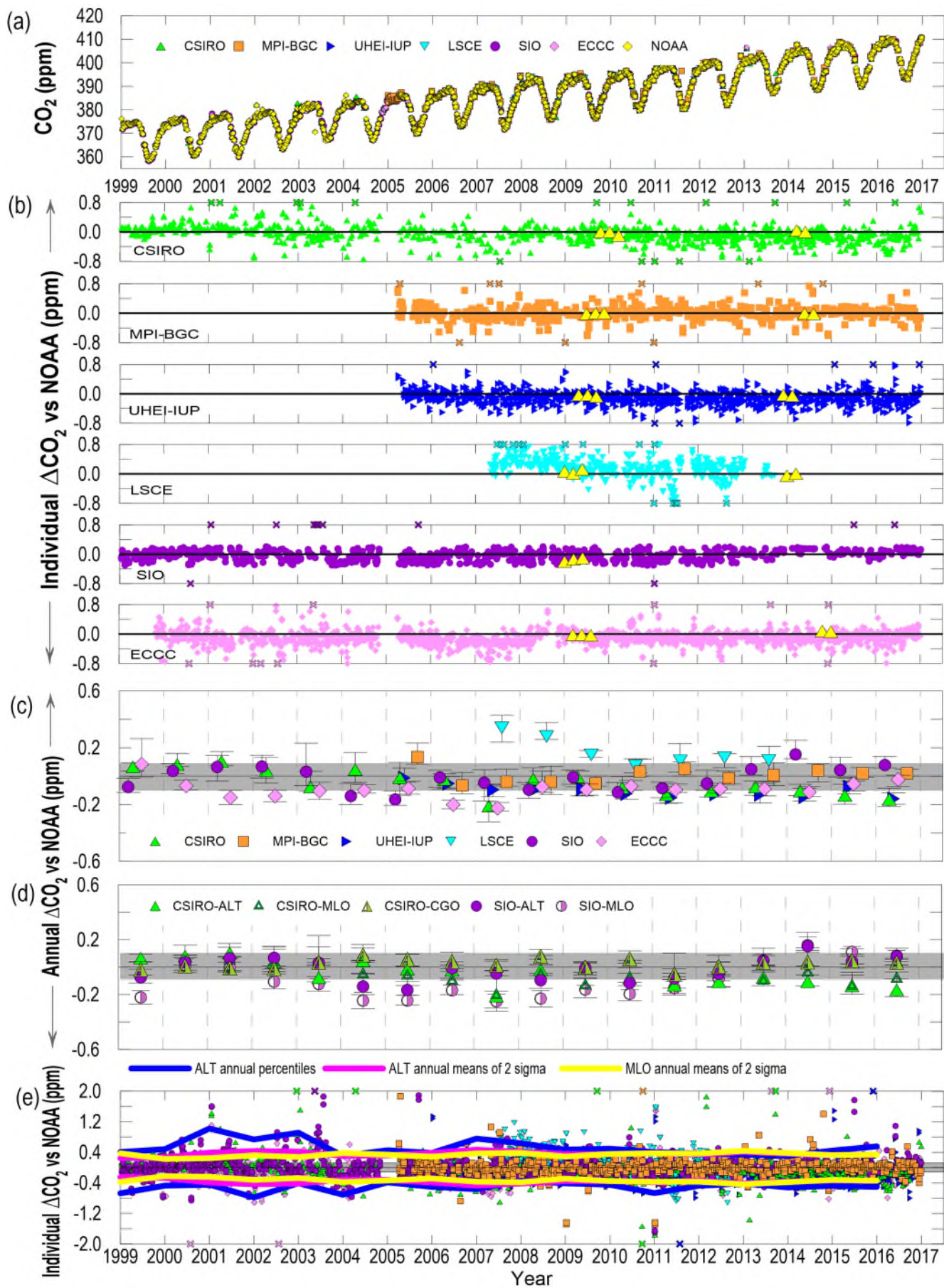
Figure 1 Atmospheric CO_2 comparison results, in ppm, from flask samples taken at Alert, Canada (ALT), Mauna Loa, USA (MLO) and Cape Grim, Australia (CGO) by seven laboratories (CSIRO, MPI-BGC, UHEI-IUP, LSCE, SIO, ECCC, and NOAA). (a) Time series of each laboratory's measurements at ALT, showing long-term trends and seasonal patterns in the records. (b) Individual ALT CO_2 measurement differences (laboratory minus NOAA), in ppm. Differences exceeding the y-axis range are plotted with an "X" symbol on the outer axis. Results from the WMO/IAEA Round Robin experiments are overlaid in yellow triangles. The shaded grey band around the zero line, indicates the WMO/GAW recommended measurement agreement goal of ±0.1 ppm CO_2. (c) Annual median CO_2 differences (laboratory minus NOAA) at ALT in ppm, with the lower and upper limits of estimated 95% confidence intervals (CI). (d) Annual median CO_2 differences and 95% confidence limits, in ppm, of CSIRO minus NOAA at MLO and CGO, and SIO minus NOAA at MLO. Also included are results from ALT in (c). (e) Individual measurement differences (laboratory minus NOAA) at ALT, in ppm, for all the laboratories as a collective. Differences exceeding the y-axis range are plotted with an "X" symbol on the outer axis (some extreme outliers have been removed to produce the results). The annual 2.5 and 97.5 percentiles of the entire difference distribution from all laboratories at ALT are shown in blue (from -0.51 to +0.53 ppm). The pink lines show the annual means of the CO_2 ± 2-sigma variations of weekly sampling episodes at ALT (± 0.37 ppm) and the yellow lines show the annual means of the CO_2 ± 2-sigma variations of weekly sampling episodes at MLO (± 0.34 ppm).
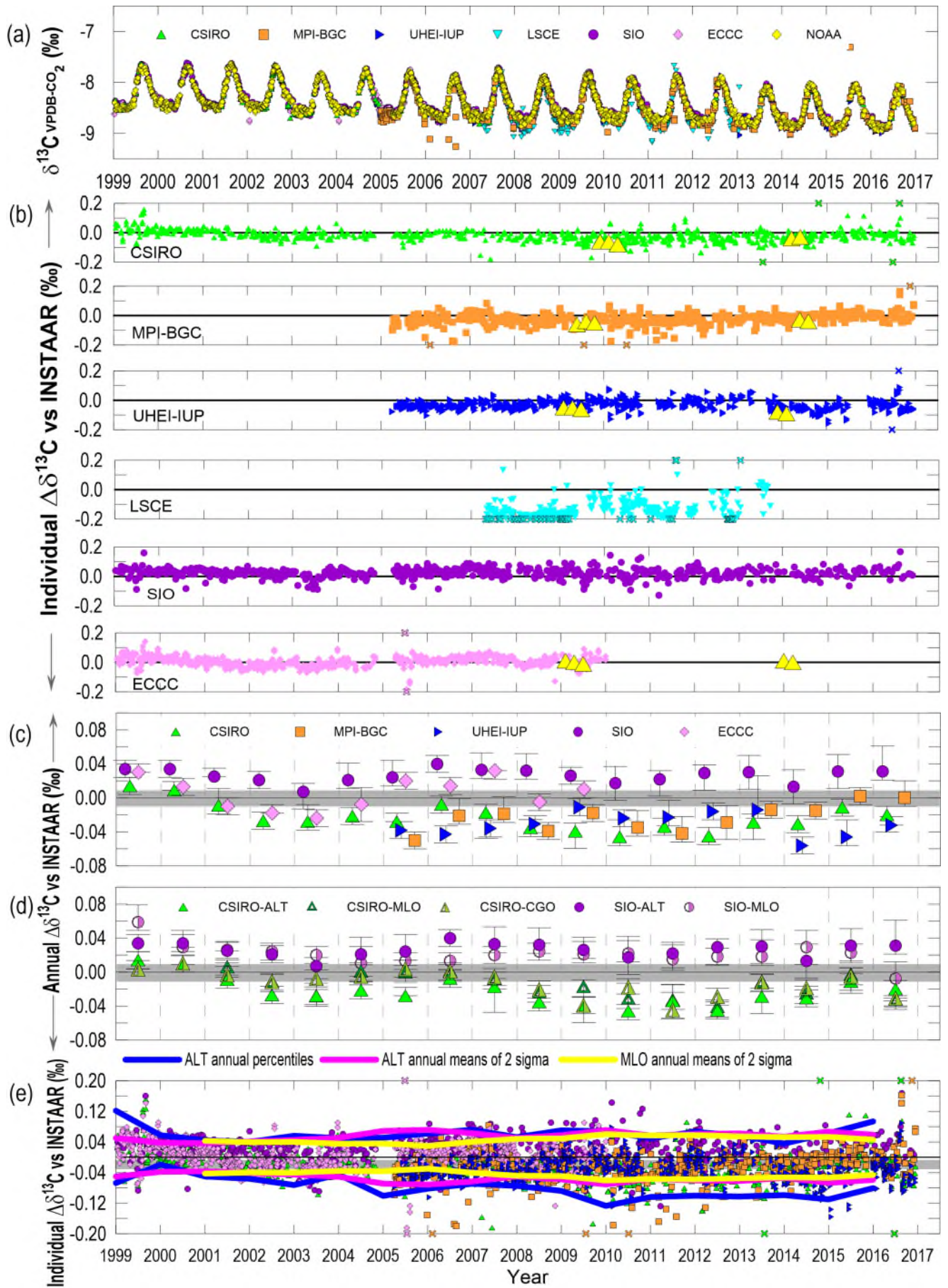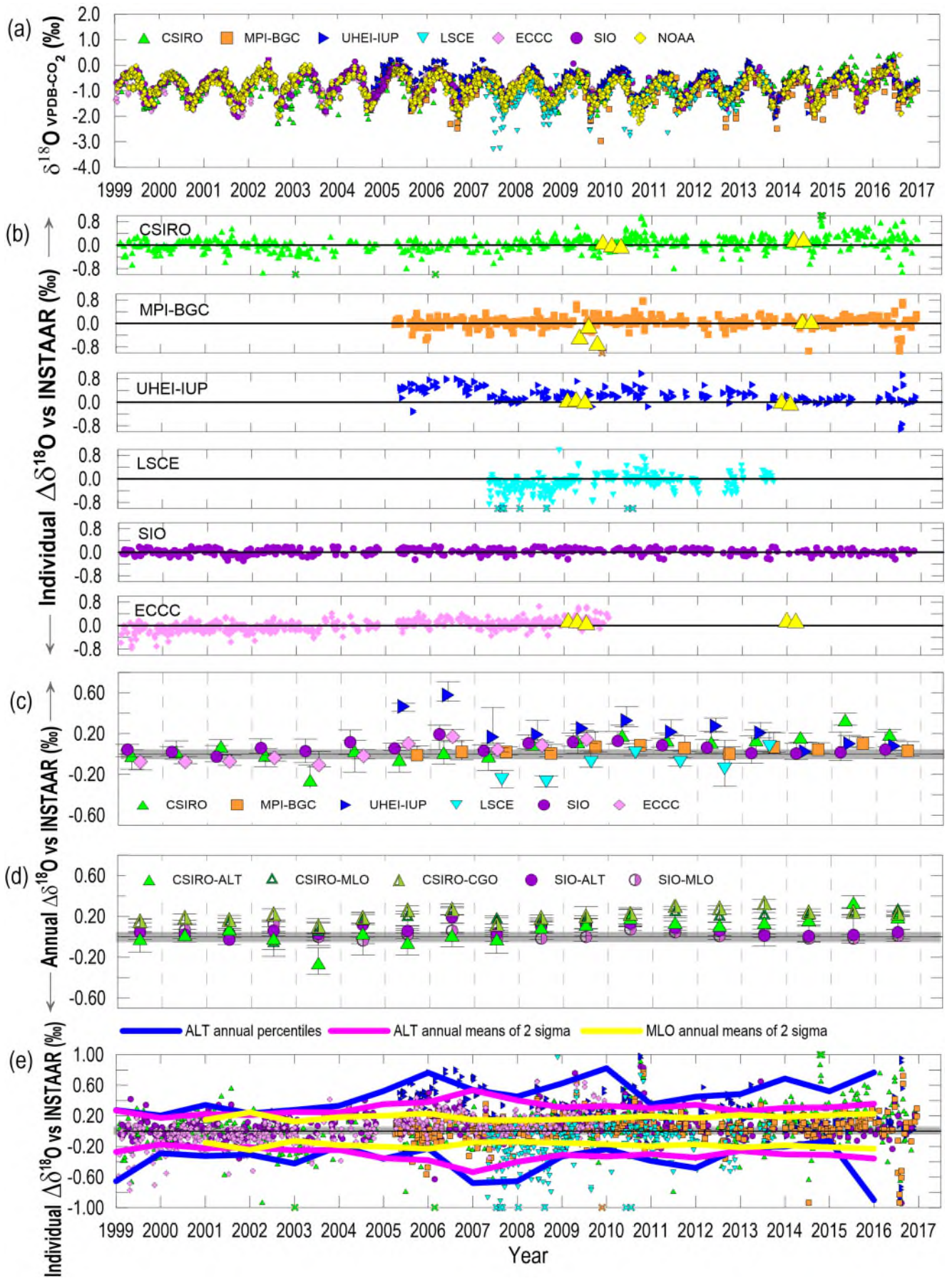
1449　**Figure 2** Atmospheric δ^{13}C-CO$_2$ comparison results, in permil (‰), from flask samples taken

1450　at ALT, MLO and CGO by seven laboratories. (a) Time series of each laboratory's

1451　measurements at ALT, showing long-term trends and seasonal patterns in the records. (b)

1452　Individual ALT δ^{13}C-CO$_2$ differences (laboratory minus INSTAAR), in ‰. Differences

1453　exceeding the y-axis range are plotted with an "X" symbol on the outer axis. Results from

1454　the WMO/IAEA Round Robin experiments are overlaid in yellow triangles. The shaded grey

1455　band around the zero line indicates the WMO/GAW recommended measurement agreement

1456　goal of ±0.01 ‰. (c) Annual median δ^{13}C-CO$_2$ differences (laboratory minus INSTAAR) at

1457　ALT in ‰, with the lower and upper limits of estimated 95% CI. (d) Annual median δ^{13}C-CO$_2$

1458　differences and 95% CI, in ‰, of CSIRO minus INSTAAR at MLO and CGO, and SIO minus

1459　INSTAAR at MLO. Also included are results from ALT. (e) Individual measurement

1460　differences (laboratory minus INSTAAR) at ALT, in ‰, for all the laboratories as a collective.

1461　Some extreme outliers have been removed to produce the results. The annual 2.5 and 97.5

1462　percentiles of the entire difference distribution from all laboratories at ALT are shown in blue

1463　(-0.09 to +0.07‰). The pink lines show the annual means of ± 2-sigma variations of weekly

1464　sampling episodes at ALT (± 0.06 ‰) and the yellow lines show the annual means of ± 2-

1465　sigma variations of weekly sampling episodes at MLO (± 0.05‰).

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Figure 3 Atmospheric $\delta^{18}O$-CO_2 comparison results, in permil (‰), from flask samples taken at ALT, MLO and CGO by seven laboratories. (a) Time series of each laboratory's measurements at ALT, showing long-term trends and seasonal patterns in the records. (b) Individual ALT $\delta^{18}O$-CO_2 differences (laboratory minus INSTAAR), in ‰. Differences exceeding the y-axis range are plotted with an "X" symbol on the outer axis. Results from the WMO/IAEA Round Robin experiments are overlaid in yellow triangles. The shaded grey band around the zero line indicates the WMO/GAW recommended measurement agreement goal of ±0.05 ‰. (c) Annual median $\delta^{18}O$-CO_2 differences (laboratory minus INSTAAR) at ALT in ‰, with the lower and upper limits of estimated 95% CI. (d) Annual median $\delta^{13}C$-CO_2 differences and 95% CI, in ‰, of CSIRO minus INSTAAR at MLO and CGO, and SIO minus INSTAAR at MLO. Also included are results from ALT. (e) Individual differences (laboratory minus INSTAAR) at ALT, in ‰, for all the laboratories as a collective. The annual 2.5 and 97.5 percentiles of the entire difference distribution from all laboratories at ALT are shown in blue (-0.50 to +0.58‰). The pink lines show the annual means of ± 2-sigma variations of weekly sampling episodes at ALT (± 0.31 ‰) and the yellow lines show the annual means of ± 2-sigma variations of weekly sampling episodes at MLO (± 0.19‰).

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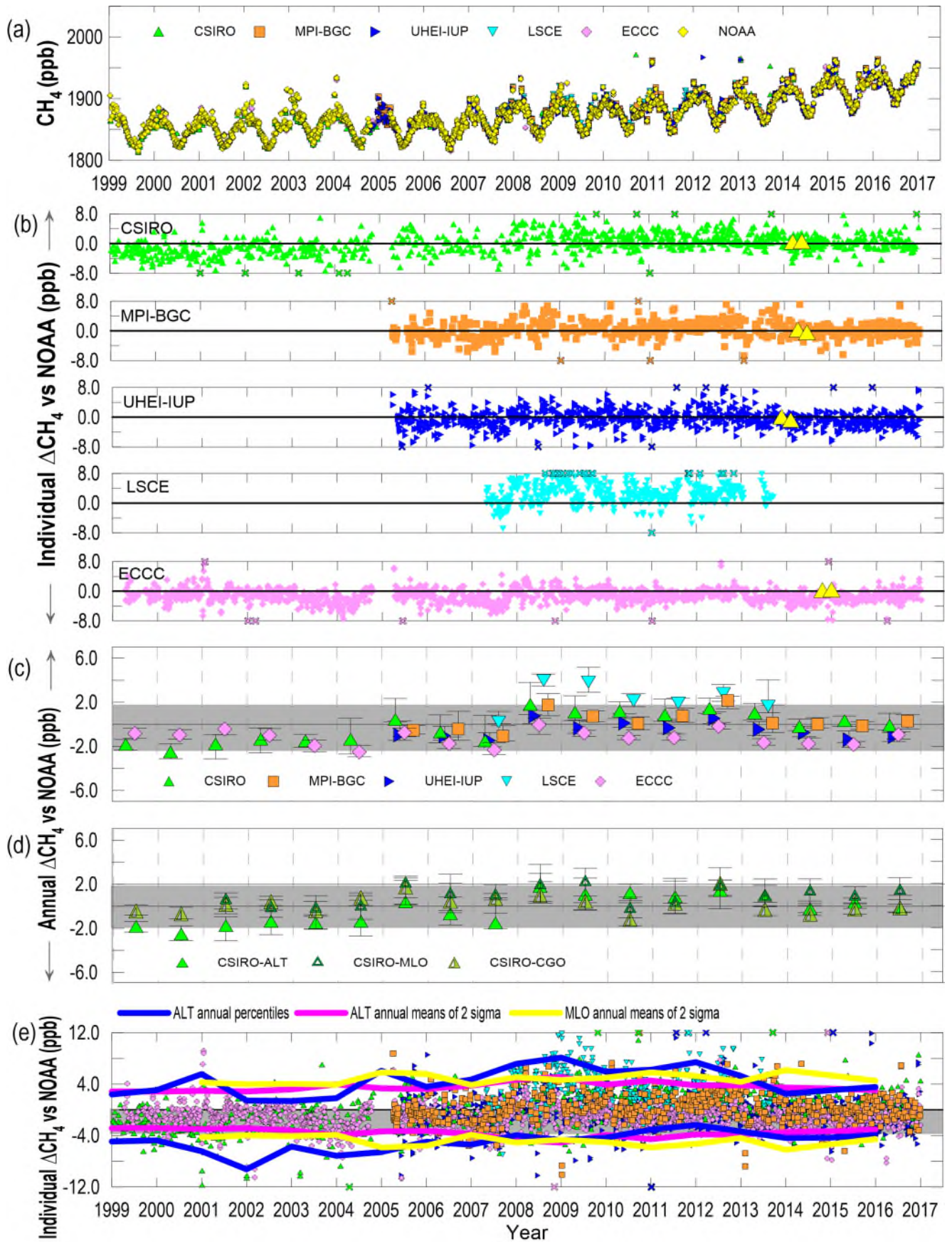
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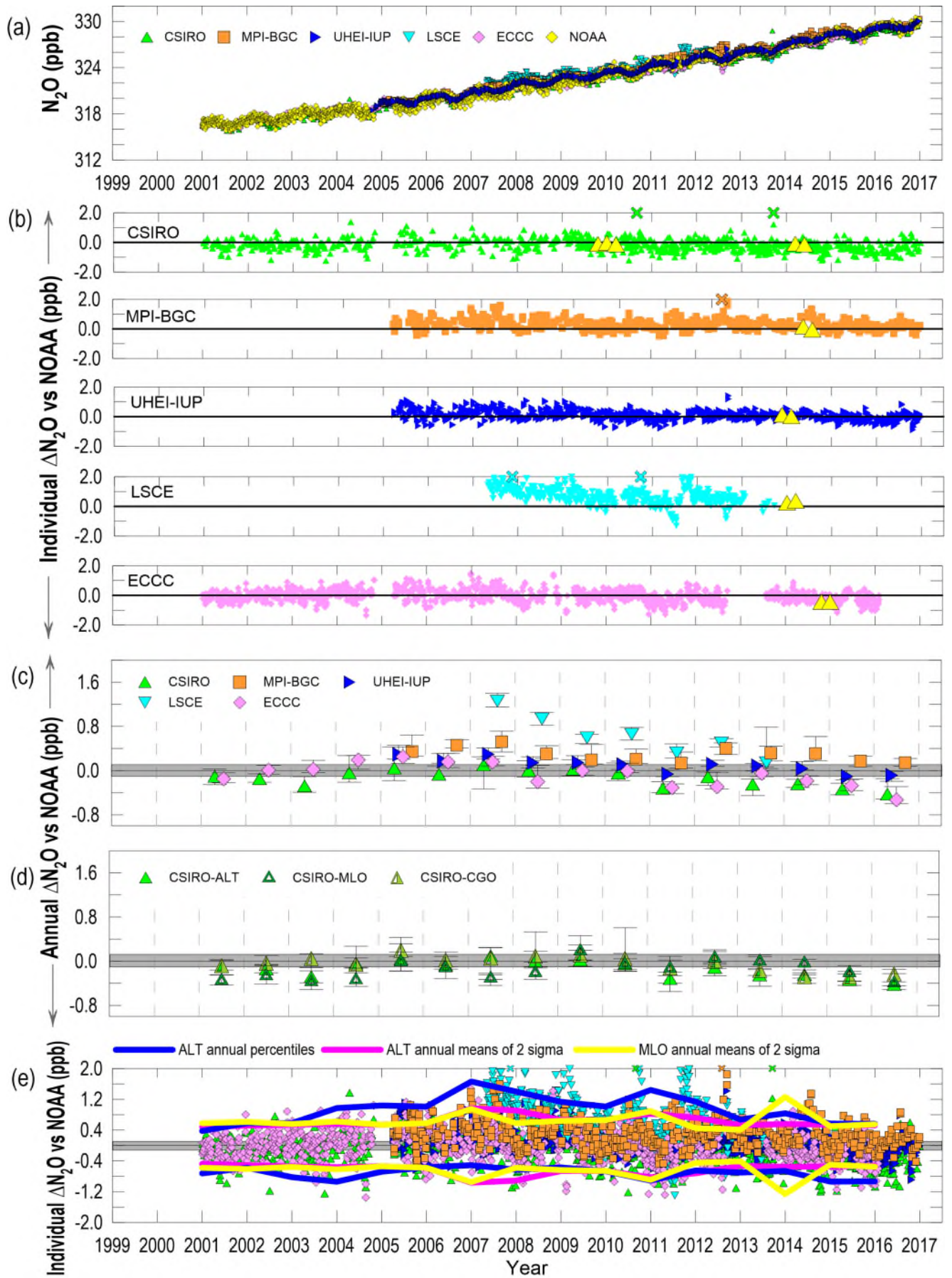**Figure 4** Atmospheric CH_4 comparison results, in ppb, from flask samples taken at ALT, MLO and CGO by six laboratories (CSIRO, MPI-BGC, UHEI-IUP, LSCE, ECCC, and NOAA). (a) Time series of each laboratory's measurements at ALT, showing long-term trends and seasonal patterns in the records. (b) Individual CH_4 differences (laboratory minus NOAA) at ALT, in ppb. Differences exceeding the y-axis range are plotted with an "X" symbol on the outer axis. Results from the WMO/IAEA Round Robin experiments are overlaid in yellow triangles. The shaded grey band around the zero line indicates the WMO/GAW recommended measurement agreement goal of ±2.0 ppb. (c) Annual median CH_4 differences (laboratory minus NOAA) at ALT in ppb, with the lower and upper limits of estimated 95% CI. (d) Annual median CH_4 differences and 95% CI, in ppb, of CSIRO minus NOAA at MLO and CGO. Also included are results from ALT. (e) Individual differences (laboratory minus NOAA) at ALT, in ppb, for all the laboratories as a collective. Some extreme outliers have been removed to produce the results. The annual 2.5 and 97.5 percentiles of the entire difference distribution from all laboratories at ALT are shown in blue (-4.86 to +6.16 ppb). The pink lines show the annual means of ± 2-sigma variations of weekly sampling episodes at ALT (± 3.62 ppb) and the yellow lines show the annual means of ± 2-sigma variations of weekly sampling episodes at MLO (± 4.88 ppb).
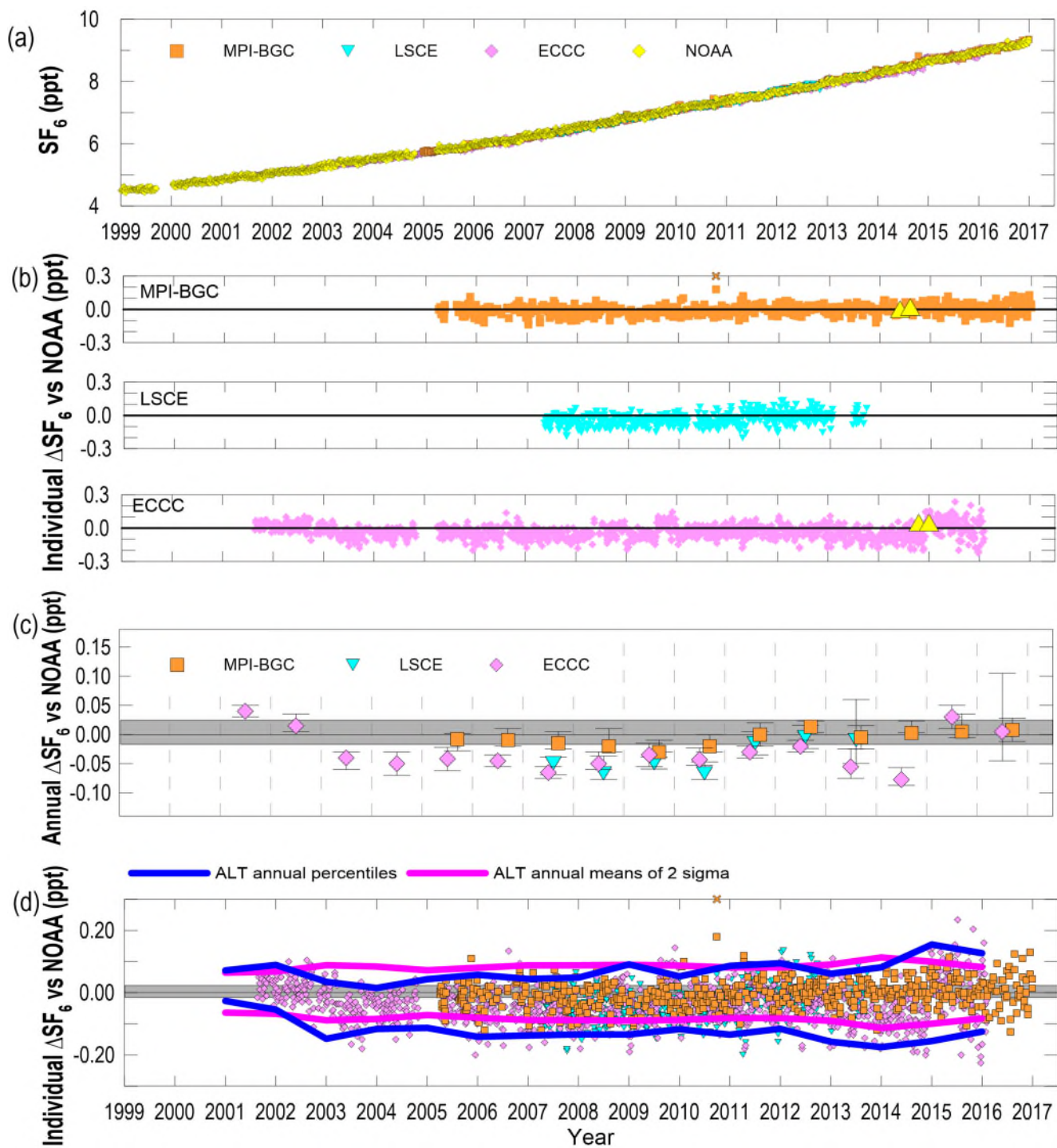
Figure 5 Atmospheric N_2O comparison results, in ppb, from flask samples taken at ALT, MLO and CGO by six laboratories (CSIRO, MPI-BGC, UHEI-IUP, LSCE, ECCC, and NOAA). (a) Time series of each laboratory's measurements at ALT, showing long-term trends and seasonal patterns in the records. (b) Individual N_2O differences (laboratory minus NOAA) at ALT, in ppb. Differences exceeding the y-axis range are plotted with an "X" symbol on the outer axis. Results from the WMO/IAEA Round Robin experiments are overlaid in yellow triangles. The shaded grey band around the zero line indicates the WMO/GAW recommended measurement agreement goal of ±0.1 ppb. (c) Annual median N_2O differences (laboratory minus NOAA) at ALT in ppb, with the lower and upper limits of estimated 95% CI. (d) Annual median N_2O differences and 95% CI, in ppb, of CSIRO minus NOAA at MLO and CGO. Also included are results from ALT. (e) Individual differences (laboratory minus NOAA) at ALT, in ppb, for all the laboratories as a collective. The annual 2.5 and 97.5 percentiles of the entire difference distribution from all laboratories at ALT are shown in blue (-0.75 to +1.20 ppb). The pink lines show the annual means of ± 2-sigma variations of weekly sampling episodes at ALT (± 0.64 ppb) and the yellow lines show the annual means of ± 2-sigma variations of weekly sampling episodes at MLO (± 0.64 ppb).

Figure 6 Atmospheric SF₆ comparison results, in ppt, from flask samples taken at ALT by
four laboratories (MPI-BGC, LSCE, ECCC, and NOAA). (a) Time series of each laboratory's
measurements at ALT, showing long-term trends and seasonal patterns in the records. (b)
Individual SF₆ differences (laboratory minus NOAA) at ALT in ppt. Differences exceeding the
y-axis range are plotted with an "X" symbol on the outer axis. Results from the WMO/IAEA
Round Robin experiments are overlaid in yellow triangles. The shaded grey band around the
zero line indicates the WMO/GAW recommended measurement agreement goal of ±0.02
ppt. (c) Annual median SF₆ differences (laboratory minus NOAA) at ALT in ppt, with the

lower and upper limits of estimated 95% CI. (d) Individual differences (laboratory minus NOAA) at ALT, in ppt, for all the laboratories as a collective. The annual 2.5 and 97.5 percentiles of the entire difference distribution from all laboratories at ALT are shown in blue (-0.14 to +0.09 ppt). The pink lines show the annual means of ± 2-sigma variations of weekly sampling episodes at ALT (± 0.09 ppt) and there is no MLO data because neither CSIRO nor SIO measure SF_6.