**SOP6: Underway measurements of methane and nitrous oxide concentrations in surface seawater**

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**1. Background**

Ship-based underway measurements of methane (CH4) and nitrous oxide (N2O) concentrations in marine surface waters are a powerful tool to study their sub-km variation across ocean basins. While the concentrations alone only give the direction of fluxes across the sea-air interface, combining concentration measurements with wind speed-based gas exchange parameterizations allows estimating the magnitude of the fluxes as well. Hence, coordinated deployments of suitable analytical systems will lead to improved estimates of marine emissions and uptake of these long-lived greenhouse gases, helping to quantify the ocean’s role in global climate change.

Up to the 1990s, most underway measurements of trace gases relied on discrete and semi-continuous analytical systems with headspace equilibration or purge-and-trap extraction techniques used in conjunction with gas chromatographs (GCs) equipped with flame ionization (CH4) and electron capture (N2O) detectors (e.g. Swinnerton and Linnenbom, 1967; Cohen, 1978; Elkins, 1980; Weiss, 1981; Butler et al., 1989; Butler and Elkins, 1991; Bange et al., 1994). Although recently developed automated gas chromatography-mass spectrometry (GC-MS) systems allow analyzing 25 samples over five hours with minimal operator involvement (Capelle et al., 2015), these GC-MS based measurements depend on a discrete sampling strategy. Such operational limitations hinder a full resolution of fine-scale features of the CH4 and N2O distributions, highlighting the clear need for high-resolution underway systems.

The development of laser infrared absorption spectroscopy techniques (see reviews by Maddaloni et al., 2006 and Friedrichs, 2008) has enabled the quantification of trace gas mole fractions with precisions better than 10-9 (1 nmol mol-1) at quasi-continuous rates (1–10 Hz), both on research vessels (e.g. Arévalo-Martínez et al., 2013; Grefe and Kaiser, 2014; Webb et al., 2016; Pohlman et al., 2017) and voluntary observing ships (VOS; e.g. Gülzow et al., 2011; 2013). With more research groups worldwide developing their own underway systems, it is crucial to develop common practices in order to ensure quality and compatibility of the results. This Standard Operating Procedure (SOP) describes methods for carrying out underway measurements of CH4 and N2O concentrations in seawater, performing calibrations, evaluating system performance and quality-controlling final data sets. While this SOP mainly focuses on high-precision surface measurements for open ocean settings with moderate gradients, we also give some recommendations for surveys in highly dynamic settings such as those found in estuarine systems and study sites in the vicinity of ground water seepage or vent fields (mainly for CH4). In these environments, high sampling frequency and resolution might be more critical for the description of the biogeochemical setting, and the considerations of accuracy (see sections 2 and 3) cannot be met. To this end, in section 5 we address the use of both membrane-based gas extraction systems and post-processing routines to overcome the response time limitation of the equilibration system (*τ* correction).

**2. Measurements**

**2.1 Measurement principle**

Irrespective of the detection and equilibration systems used (section 2.2.6), the general principle involves equilibrating air (gas phase) with a continuously running seawater stream (aqueous phase), and circulating the equilibrated air through one (or more) trace gas analyzer(s) before returning it to the equilibration system within a closed loop. Alternatively, membrane-based systems either extract gases from the water phase by a gas-permeable membrane (e.g. Troncoso et al., 2018) or equilibrating the gases in the water phase with a gaseous headspace via a semi-permeable membrane (e.g. Canning et al., 2020). Most analyzers based on laser spectroscopy report the mole fractions of CH4 and/or N2O in the gas phase as dry equivalents using an infrared H2O absorption line to correct for the water vapor mole fraction, *x*meas(H2O), in the gas mixture:

*x*dry(gas) = *x*meas(gas) / [1 – *x*meas(H2O)] Eq. 1

**2.2 Hardware**

To date there is no consensus as to which specific components offer an optimum performance for all circumstances since this strongly depends on the particular application (environmental setting, attended or unattended operation). Hence, the equipment described here represents a compilation of commonly used systems as identified by the SCOR WG # 143. It is, however, generally recommended to use gas-tight, chemically inert tubing as well as gas-tight pipe fittings (e.g. Swagelok) when assembling the gas lines conducting sample air through the analytical system.

**2.2.1 Water supply**

For ship-based applications, water is drawn from 2–10 m depth by either using a submersible pump installed in the vessel’s hydrographic well (so-called “moonpool”), the ship’s scientific seawater supply system, whose intake is often located near the bow, or using the sea-chest (cooling water intake for the ship’s engines). As seawater is transported from the intake point to the equilibration system, temperature changes can take place, which may change the partial pressure of the dissolved gases compared with in-situ conditions. Hence, these temperature-driven changes need to be accounted for when processing the data (section 4). To reduce the temperature changes, it is recommended to insulate and minimize the length of the pipeline. Thermal insulation might be particularly useful if long pipes cannot be avoided, as in, for instance, long-term installations on board VOS. The water flow rate depends on the specific requirement of the equilibration system (typically 2–6 L min-1), but it is recommended to keep a higher flow than needed by the system (e.g. by using a bypass) to reduce the transit time between the intake and equilibrator (see Pierrot and Steinhoff, 2019). The transit time from the ship intake to the equilibrator can be taken into account by subtracting the transit time from the recorded time of each measurement (Pohlman et al., 2017).

Organic matter accumulation caused by bacterial biofilms could result in production of trace gases within the water lines. To avoid this interference, routine treatment of the water lines and thorough flushing is recommended (see e.g. Juranek et al., 2010).

**2.2.2 Air supply**

Most studies of the surface seawater distribution of CH4 and N2O aim to estimate the concentration difference between the ocean and the overlying atmosphere for computing sea-air fluxes (also known as flux densities; unit symbol: kg m–2 s–1 or mol m–2 s–1; see e.g. Wanninkhof, 1992; Wanninkhof, 2014). To sample atmospheric air, a sampling line is installed at the ship’s mast or bow to minimize contamination from the engine’s exhaust. A commonly used material used for this purpose is Synflex (also known as Dekoron and Dekabon) tubing (Eaton, Ireland) with an outer diameter between 6 and 14 mm (inner diameter 4–10 mm). Synflex 1300 is a rugged, flexible and chemically inert aluminium/plastic composite tubing. Sample air is pumped to the analytic system, which may be located near the mast or in an interior laboratory space. In some cases, the analyzer used for measuring the mole fractions in seawater is mode-switched to alternate between equilibrator (or membrane system) and air. If the air handling system does not have a gas dryer, moisture from the seawater-extracted gas must be flushed before the atmospheric measurement is recorded. Ship exhaust emissions as well as other sources such as ship’s lavatories, fuel stores, and personnel can influence the air measurements. For this reason, air sampling should take into account the relative wind direction and relative wind speed at the time of sampling. The precise sector for obtaining acceptable data will vary with the structure of the ship and mast (or other sampling location) where the air is collected. Generally, relative wind directions ± 120º from the ship’s forward vector and wind speeds > 2 m s-1 are safe from ship contamination, although variations may occur depending on the specifics of the installation. In near-coastal studies, atmospheric contamination from upwind land point sources may additionally become an issue.

**2.2.3 Reference gases**

Different gas analyzers have distinct requirements in terms of the number of reference gases used for internal calibration. Nevertheless, it is recommended to carry out regular measurements of at least 2 non-zero reference gases which bracket the expected mole fractions in the area of interest. While such gas mixtures with different mole fractions of CH4 and N2O are commercially available from several providers, it is crucial to ensure that these reference gases are calibrated against high-quality standards that can be traced back to NOAA GMD (National Oceanographic and Atmospheric Administration - Global Monitoring Division) or WMO (World Meteorological Organization) scales. For studies of dissolved CH4 and N2O concentrations far from atmospheric saturation equilibriums (e.g. vicinity of gas seeps, estuaries, coastal upwelling regions) this might not be possible because it would require using reference gases out of the range covered by the NOAA GMD or WMO primary standard scales. In view of this issue, the SCOR Working Group # 143 produced a set of primary standards with mole fractions in the range of 4.5–4.8 µmol mol–1 for CH4 and 22–24 µmol mol–1 for N2O (Bullister et al., 2016). These standards were distributed to twelve laboratories around the world to facilitate their wide-spread use (see SOP4). Standard operating procedures for gas handling during the calibration process can be found in SOP2.

Instrumental drift over time varies depending on the analyzer used, making the calibration frequency user-dependent. While it has been customary to measure standard gases every 6–8 hours in the CO2 community to account for the drift of classical infrared detectors (Pierrot et al., 2009), modern sensors based on cavity enhanced absorption spectroscopy are often more stable, which justifies measuring reference gases less frequently, e.g. once per day. In any case, it is recommended to aim for a maximal drift which does not exceed the WMO's compatibility targets for atmospheric CH4 (± 2 nmol mol–1) and N2O (± 0.1 nmol mol–1) mole fractions (Tans and Zellweger, 2014).

**2.2.4 Detection system**

Commercially available high-quality analyzers for CH4 and/or N2O mole fractions obtain short-term precisions (<10 s) below 0.1 nmol mol–1. Some analyzers simultaneously measure CH4 and N2O, whereas others measure either one or the other, often in combination with trace gases such as CO2 or carbon monoxide (CO). Irrespective of the combination, all analyzers also measure the water vapor mole fraction of the sample gas, *x*meas(H2O). The most commonly used trace gas analyzers for continuous measurements of CH4 and N2O are based on either cavity ringdown spectroscopy (CRDS; O’Keefe et al., 1998), off-axis integrated cavity output spectroscopy (OA-ICOS; Baer et al., 2002), or Fourier transform infrared spectroscopy (FTIR; Griffiths and de Haseth, 2007). Details on the individual measurement techniques can be found in the respective references. Some of the sensors for multiple gases might not perform equally well in terms of the recommended compatibility targets (see above) and therefore this should be considered when setting up the analytical system.

**2.2.5 Drying system**

The presence of water vapor in the sample gas stream (equilibrated air being directed through the analyzer) alters the measured mole fractions of CH4 and N2O due to dilution and, in some cases, absorption band broadening effects. Most spectroscopic analyzers report water vapor-corrected (dry) gas mole fractions (section 2.1), and high-precision, instrument-specific water vapor corrections can be employed (Rella et al., 2013). However, better accuracy and precision can be obtained by drying the air stream exiting the equilibration system, which also reduces the possibility of condensation inside the tubing connected to the analyzer. Therefore, complete or partial drying is a common practice for measurements that involve gas equilibrators. The drying procedure can be performed by cooling the gas stream (e.g. with a cryogenic trap), using a chemical drying agent (e.g. magnesium perchlorate, Mg(ClO4)2), including a drying membrane (Nafion) in the sample gas line, or a combination of these measures.

**2.2.6 Equilibration system**

Measuring mole fractions of CH4 and N2O in a continuous fashion as outlined by this SOP requires the analyte (sample) to be in gaseous rather than dissolved form. To this end, a wide variety of either commercially available or custom-made equilibration devices are routinely used by several groups. These devices use different methods to achieve equilibrium between the gaseous and water phase (Table 1) and there have been comparison studies to test their performance for various trace gases (Körtzinger et al., 1996; Webb et al., 2016). Since the equilibration method depends on the application, detection system and available seawater supply rate, we do not intend to argue in favor of a particular equilibration device/technique. However, the general recommendation is that the system of choice increases the exchange surface between gas and water phases as much as possible, and that it has a water/gas ratio that allows for equilibration times that are adequate for the intended spatial and temporal resolution of the area under study. To avoid pressure-driven alterations of the gas phase in the equilibrator, it is recommended to operate it at ambient pressure by means of a vent. Potential biases resulting from air exchange through the vent (i.e. between the equilibrator and surrounding air) can be reduced by connecting it to a pre-equilibrator, which effectively dampens any gas loss from the main equilibrator (see e.g. Pierrot et al., 2009).

The equilibration process between gas and water phases for a given trace gas is mostly dependent on factors such as the equilibration technique, water flow, and the solubility of the species of interest (Johnson, 1999). Furthermore, temperature and salinity of the sample stream influence its bubble size distribution, which, in turn, might affect the equilibration time of a given system. The time constant of the equilibrator (*τ*), defined as the time interval needed for a given concentration difference between water and gas phases to decrease exponentially to 1/e of the initial value, is commonly used as an indicator of the equilibration system performance. Knowing the response time of an equilibrator is necessary for an adequate interpretation or correction of data that stems from dynamic settings, i.e. where the observation period over which concentrations are changing is not significantly greater than the response time of a given system (see 5). Time constants are calculated from laboratory or field-based experiments that measure the exponential rise and decay of gas concentrations during the transition from lower to higher (rise) and higher to lower (decay) concentrations. An exemplary experimental set-up using a cavity enhanced laser absorption spectrometer coupled to an equilibrator system supplied with ambient air-equilibrated and trace gas-enriched water reservoirs is found in Webb et al. (2016). For details on the computation of *τ* the reader is referred to that publication. Equilibration response times reported in published literature range between 10 and 41 min for CH4 and 1 and 6 min for N2O (Table 1).

**Table 1.** Measured time constants for equilibration systems used for the determination of CH4 and N2O.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Equilibration device/technique** | **Gas** | **Response time *τ*/min** | **Water flow *F*/(L min-1)** | **Reference** |
| Bubble-type | CH4 | 11.3 | 0.51 | Gülzow et al. (2011) |
| Passive membrane | CH4 | 22 | 7 | Canning et al. (2020) |
| Weiss-type | CH4 | 10–20 | 20 | Pohlman et al. (2017) |
| Weiss-type | CH4 | 36–41 | 3 | Li et al. (2015) |
| Weiss-type | CH4 | 158 | 13–20 | Johnson (1999) |
|  | N2O | 6.4 |
| Weiss-type | CH4 | 20 | 24–30 | Rhee et al. (2009) |
|  | N2O | 1 |
| Weiss-type | N2O | 2.4 | 2 | Arévalo-Martínez et al. (2013) |
| Glass-bed | N2O | 2.4 | 1.8 | Grefe and Kaiser (2014) |

**3. Procedure**

In the following, a measurement sequence for analysis of CH4 and N2O based on the principles described above is presented. While the exact order in which these steps are carried out, as well as the frequency, is user (i.e. application) dependent, it is recommended to adhere to the standard procedures in terms of analytical drift and calibration targets to ensure comparability of the results.

**3.1 Measurement circuits**

The analytical setup described in this SOP concerns both atmospheric and seawater measurements. Given that the gas sample stream from the equilibrator is run as a closed loop (see section 2.1), it is critical to isolate this gas circuit from those conducting atmospheric air and reference gases to the gas analyzer, such that the latter are discarded after the measurements have been carried out.

**3.2 Calibration of the gas analyzer**

Most spectroscopic analyzers used for underway measurements of CH4 and N2O require 1 to 3 reference gases to perform a calibration. The frequency of this procedure is highly dependent on the particular instrument and should be adjusted to match to the targets in section 2.2.3. It is recommended to flush the analyzer's cavity thoroughly with a given reference gas before performing the calibration.

**3.3 Leak test**

Equilibrator-based analysis systems are operated under the assumption that the system is sealed, or not actively exchanging air with the atmosphere. In reality, systems that include pumps for circulating gas between the analyzer and the equilibrator, numerous fittings that connect system components, and analyzers not specifically designed to be leak-free will have a measurable exchange rate with the exterior air. The effect of exchange between the system and the atmosphere is that chemical equilibrium is not achieved. Because the oceans are almost always at or above saturation with respect to CH4 and N2O (Wilson et al., 2020), the outcome of gas exchange is an underestimation of surface water gas concentrations and their potential environmental impact. To minimize the effect of this exchange, most equilibrators are equipped with an intake connected to a secondary equilibrator such that any gas lost from the system is replaced by pre-equilibrated gas. However, because the capacity of the secondary equilibrator to maintain system equilibrium is limited, a system leak test to quantify gas exchange between the analytical system and the atmosphere is a critical component of a system’s installation and operation.

A leak test is conducted by isolating the equilibrator from the atmosphere, injecting a standard with a gas mole fraction significantly greater than that in ambient air, and then monitoring the rate at which the mole fraction drops. The water seal at the base of the equilibrator is a sufficient isolation and the enriched gas may be introduced through the vent intake. Assuming first-order concentration-dependent exchange, the turnover time for gas within the analytical system is calculated by dividing the internal gas concentration by a one-minute averaged rate of gas loss from the system. To achieve consistent results for CH4 concentrations determined from discrete samples obtained from incoming water and those from the equilibrator headspace, the ratio of the system turnover time and *τ* should be greater than 50 (Pohlman et al., 2017). In that case, the gas exchange rate will not have a meaningful effect on CH4 concentrations in the equilibrator. A leak test must be conducted as part of every installation, and periodic leak tests are recommended during prolonged field programs for data quality assurance. The most robust method to assure a system has an acceptable leak rate or is generally performing well is to directly compare the equilibrator-based values against discrete measurements of the water supplying the equilibrator. However, lacking a discrete sample analysis system at the installation site, an evaluation of the turnover time to *τ* ratio is sufficient.

**3.4 Measurement cycle**

After initial calibration, the analytical system can be set up to alternate between seawater, atmospheric and reference gas measurement circuits. To this end, a manual or electronically controlled valve system can be used. The advantage of the latter is a more precise control of the timing of the different circuits as well as longer periods of unattended operation. Furthermore, electronic control coupled to a data logging system can be configured to add flags to the different measurement circuits, which facilitates data post-processing (section 4).

Depending on the specific application, a common measurement cycle for underway CH4 and N2O includes a 15–30 min period of atmospheric measurements followed by 6–8 h of seawater measurements, after which atmospheric measurements can be repeated. Several systems include control measurements (5–15 min) of 1 to 3 reference gases directly after the atmospheric and seawater measurements to both monitor instrumental drift and assess whether a new calibration is required (section 2.2.3). Care should be taken that enough flushing time is allowed after changing between the different measurement circuits in order to avoid mixture of, for instance, reference gases and equilibrated sample gas within the analyzer’s cavity.

In coastal systems with high water and/or land sources the atmospheric CH4 and N2O mole fractions may be locally enhanced and more variable. Thus, more frequent atmospheric measurements might be needed depending on the study’s goals. However, it should be considered that due to the usually longer equilibration time for CH4 (Table 1), frequent air measurements might result in a loss of data coverage for seawater measurements because of the time that is needed for the system to re-equilibrate. Hence, in remote marine atmospheric boundary layers where atmospheric CH4 and N2O mole fractions show little variability, it may be preferable to compromise the atmospheric measurements for the sake of continuously recording seawater. An optimal, yet costly, solution for this problem is to measure equilibrated seawater and atmospheric air in separate analyzers running simultaneously.

**3.5 Operating several gas analyzers simultaneously**

Often underway measurements of CH4 and N2O are conducted in combination with systems capable of measuring other climate-relevant trace gases (e.g. CO2). To this end, coupling more than one gas analyzer might be needed. Given that most routinely used spectroscopic analyzers include both internal pumps that drive the gas flow through their cavity, and pressure controllers that maintain the required flow through the system, it is important to make sure counteracting gas flows are avoided. Hence, running two or more analyzers requires either to connect the outlet of one analyzer to the inlet of the next (installation in series), or to use a tee fitting and feed both analyzers from the same air stream (installation in parallel). Running analyzers in series can be advantageous in that standard gases can be used more efficiently. However, should one of the internal pumps develop a leak, it will be challenging to quickly establish which one it is. If an installation in parallel is chosen, care should be taken that the length of the gas lines is reduced as much as possible to avoid time differences between the signals detected by the analyzers. Another aspect to consider is that using multiple sensors on a common equilibration system leads to extended equilibration time constants, because the total circulating gas volume increases, while the amount of gas in the equilibrator (i.e. actively equilibrating), stays the same. Therefore, when setting up an analytical system with multiple sensors, it is important to consider the dimensions and exchange behavior of the equilibrator as well.

**4. Data post-processing**

**4.1 Auxiliary data**

Other measurements are critical for the actual calculation of dissolved gas concentrations, and/or sea-air fluxes of CH4 and N2O. Temperature and pressure within the equilibrator should be monitored with accuracies better than 0.01 K and 0.5 hPa, respectively. Furthermore, temperature measurements of the same high-quality as well as salinity data (accuracy better than 0.05) from the seawater intake are required. Meteorological and navigation data of sufficient accuracy may be available from the ship’s operational equipment/data distribution system (in particular on research vessels). This data should include: atmospheric pressure normalised to sea level, true wind speed and direction, and if possible, ship orientation, direction of travel and speed.

Before proceeding with the computation of gas concentrations and/or fluxes, it is important to make sure that the time stamps of the analyzer(s) match those of the auxiliary data. This can be done either in beforehand by setting up a data logging system that retrieves data from all sensors and delivers a combined output, or after the campaign by adjusting the timestamps of e.g. the ship’s data distribution system and the obtained raw files from the trace gas analyzer(s) and other devices. While the computation of CH4 and N2O concentrations is described in detail in the following section, for the computation of sea-air fluxes the reader is referred to Nightingale (2009) and Wanninkhof (2014)

**4.2 Computation of concentrations**

Trace gas concentrations (*c*) are calculated from measured dry mole fractions (*x*dry) using the solubility function *F* at equilibrator temperature *T*eq:

*c* = *x*dry *F*(*T*eq,*S*) *p*eq  Eq. 2

where *T*eq is the equilibrator temperature, *p*eq is the equilibrator pressure, and *S* is practical salinity. The resulting errors of using these instrumental accuracies is shown in Table 2.

**Table 2.** Estimated relative concentration errors associated with recommended instrumental accuracy for temperature (*T*eq) and pressure (*p*eq) measurements in the equilibrator, and sea surface salinity (*S*). The signs of the errors correspond to the sign of the bias in accuracy.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Recommended accuracy** | **Δ*c*(CH4)/*c*(CH4)** | **Δ*c*(N2O)/*c*(N2O** |
| *T*eq | ±0.01 K | ∓0.032 % | ∓0.042 % |
| *p*eq | ±0.5 hPa | ±0.050 % | ±0.050 % |
| *S* | ±0.05 | ∓0.040 % | ∓0.040 % |

The solubility function *F* for CH4 and N2O (Eq. 3a and 3b, respectively) is parameterized as:

ln[*F*(CH4,*T*,*S*)/(mol kg–1 atm–1)] = *A*1 + *A*2 (100 K/*T*) + *A*3 ln[*T*/(100 K)] + *A*4 [*T*/(100 K)]

+ *S* [*B*1 + *B*2 [*T*/(100 K)] + *B*3 [*T*/(100 K)]2] Eq. 3a

ln[*F*(N2O,*T*,*S*)/(mol kg–1 atm–1)] = *A*1 + *A*2 (100 K/*T*) + *A*3 ln[*T*/(100 K)] + *A*4 [*T*/(100 K)]2

+ *S* [*B*1 + *B*2 [*T*/(100 K)] + *B*3 [*T*/(100 K)]2] Eq. 3b

where *T* is absolute temperature on the 1968 International Practical Temperature Scale IPTS-68 and *S* is practical salinity on the 1978 Practical Salinity Scale PSS-78. *T* is calculated from Celsius temperature (*t*68) via:

*T*/K = *t*68/ºC + 273.15 Eq. 4

The readings of a thermometer calibrated on the 1990 International Temperature Scale ITS-90 (Saunders, 1997) are converted to the IPTS-68 scale using the relationship:

*t*68 = 1.00024 *t*90  Eq. 5

The parameters for Eq. 3a and Eq. 3b are given in Table 3. The microgasometric measurements of the *F*(CH4) parameterization have an accuracy of ± 0.5 % (Yamamoto et al., 1976), and the root-mean-squared deviation of the fit equation for *F* to the underlying data is ± 0.48 % (Wiesenburg and Guinasso, 1979). The relative accuracy of *F*(N2O) is estimated to be ± 0.3 %, and its precision is given as ± 0.1 % (1 standard deviation; Weiss and Price, 1980).

**Table 3.** Coefficients for the computation of *F*(CH4) (–2 ≤ *t* ≤ 30 ºC and 0 ≤ *S* ≤ 40; Wiesenburg and Guinasso, 1979) and *F*(N2O) (0 ≤ *t* ≤ 40 °C and 0 ≤ *S* ≤ 40; Weiss and Price, 1980) with Eq. 3a and Eq. 3b, respectively (both in mol kg–1 atm–1).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | ***A*1** | ***A*2** | ***A*3** | ***A*4** | ***B*1** | ***B*2** | ***B*3** |
| CH4 | –417.5053 | 599.8626 | 380.3636 | –62.0764 | –0.064236 | 0.034980 | –0.0052732 |
| N2O | –168.2459 | 226.0894 | 93.2817 | –1.48693 | –0.060361 | 0.033765 | –0.0051862 |

The parameterization for *F* already includes a water vapor correction (assuming a relative humidity of 100 %) and assumes a total pressure of *p*⦵ = 1 atm = 1013.25 hPa. If the equilibrator pressure (*p*eq) deviates from *p*⦵, a small correction must be applied to Eq. 3:

*c* = *x*dry *F*(*T*eq,*S*) *p*eq [1 − *p*vap(*T*eq,*S*)/*p*eq] / [1 − *p*vap(*T*eq,*S*)/*p*⦵] Eq. 6

The correction term (following *p*eq in Eq. 6) is between 0.9998 at *p*eq = 970 hPa and 1.0002 at *p*eq= 1050 hPa for temperatures between −2 and 30 ºC (Grefe and Kaiser, 2014). This correction of less than ± 0.02 % is usually negligible.

The water vapor pressure is calculated using:

ln[*p*vap/*p*⦵] = 24.4543 – 67.4509 (100 K/T) – 4.8489 ln[*T*/(100 K)] – 0.000544 *S*Eq. 7

as derived by Weiss and Price (1980), with a parameterization uncertainty of ± 0.5 Pa. *T* is absolute temperature on the 1968 International Practical Temperature Scale IPTS-68, and *S* is practical salinity on the 1978 Practical Salinity Scale PSS-78.

While the partial pressures of the dissolved gases change in response to temperature, the derived concentrations (in nmol kg–1) are equal to those in the seawater at the point of intake (as long as there are no inadvertent changes between intake and equilibrator, e.g. due to leaks, fouling or mixing with stale reservoirs).

**4.3 Example calculation**

**Measurement data:**

*x*meas(CH4) = 1912 nmol mol–1 (1 nmol mol–1 = 10–9)

*x*meas(N2O) = 332.2 nmol mol–1

*x*meas(H2O) = 28002 µmol mol–1 (1 µmol mol–1 = 10–6)

*t*eq = 25.12 ºC (ITS-90 scale)

*p*eq = 1012.3 hPa

*S* = 35.08

**Conversion of temperature on ITS-090 scale to absolute temperature on IPTS-68 scale:**

*T*eq = (1.00024 *t*eq + 273.15) K = (25.126 + 273.15) K = 298.276 K

**Calculation of dry mole fraction of trace gases:**

*x*dry(CH4) = *x*meas(CH4) / [1 – *x*meas(H2O)] = 1967 nmol mol–1

*x*dry(N2O) = *x*meas(N2O) / [1 – *x*meas(H2O)] = 341.8 nmol mol–1

**Calculation of solubility function at equilibrator temperature and salinity:**

*F*(CH4,*T*eq,*S*) = *F*(CH4,298.276 K,35.08) = 0.001074 mol kg–1 atm–1

*F*(N2O,*T*eq,*S*) = *F*(N2O,298.276 K,35.08) = 0.01952 mol kg–1 atm–1

**Calculation of trace gas concentrations:**

Using Eq. 2 (including conversion of pressure units)

*c*(CH4) = *x*dry(CH4) *F*(CH4,*T*eq,*S*) *p*eq

= 1967 nmol mol–1 × 0.001074 mol kg–1 atm–1 × 1012.3 hPa × 1 atm / (1013.25 hPa)

= 2.1100 nmol kg–1

*c*(N2O) = *x*dry(N2O) *F*(N2O,*T*eq,*S*) *p*eq

= 341.8 nmol mol–1 × 0.01952 mol kg–1 atm–1 × 1012.3 hPa × 1 atm / (1013.25 hPa)

= 6.6643 nmol kg–1

Using Eq. 6 (including conversion of pressure units)

*p*vap(*T*eq,*S*) = *p*vap(298.126 K,35.08) = 3129 Pa = 31.29 hPa

*c*(CH4) = *x*dry(CH4) *F*(CH4,*T*eq,*S*) *p*eq [1 − *p*vap(*T*eq,*S*)/*p*eq] / [1 − *p*vap(*T*eq,*S*)/*p*⦵]

= 2.1100 nmol kg–1 × 0.969086 / 0.969115

= 2.1100 nmol kg–1 × 0.99997

= 2.1099 nmol kg–1

*c*(N2O) = *x*dry(N2O) *F*(N2O,*T*eq,*S*) *p*eq [1 − *p*vap(*T*eq,*S*)/*p*eq] / [1 − *p*vap(*T*eq,*S*)/*p*⦵]

= 6.6643 nmol kg–1 × 0.99997

= 6.6641 nmol kg–1

**4.4 Data reporting**

Consistent data reporting is essential for compatibility of data sets obtained by different groups, and of key importance for the establishment of global data products. To this end, it is recommended that all data sets reporting underway CH4 and N2O concentrations (in nmol kg-1) are accompanied by equilibration temperature and pressure, in-situ temperature and salinity, atmospheric pressure (normalised to sea level), and if possible, true wind speed and direction (with height of the anemometer/sensor), as well as ship speed (all using SI units). Metadata including position (latitude and longitude) and UTC date and time are also required. Specific recommendations for reporting underway measurements of dissolved CH4 and N2O can be found in SOP7.

**5. Considerations for highly dynamic settings**

**5.1 Membrane systems**

The equilibration systems described above have been successfully applied in diverse deep open ocean and shallow coastal settings. However, when working in smaller areas such as methane seeps on the order of 100–200 m diameter, these customary equilibrators cannot maintain chemical equilibrium within the headspace of the equilibrator where surface water concentrations rapidly change. In such situations, faster-response but lower accuracy membrane-based instruments may be more effective for mapping the gas concentrations over small spatial scales.

**5.2 Tau (*τ*) correction**

In strict sense, the gas phase of an equilibrator will never reach full equilibration in waters with changing dissolved gas concentrations over time, but it will rather approach equilibrium with a response time (*τ*) that is specific for a given set up, temperature, salinity, air and water flow, and the gas under consideration. Though there is a general agreement that *τ* is longer for less soluble gases (see e.g. Schneider et al., 2007), the ratio of *τ* for different gases and the magnitude of the time constant for the direction of concentration range can be dependent on the set up (Webb et al., 2016). The need for quantification of sensor response time has long been recognized for profiling sensor-based applications, and algorithms have been introduced (e.g. Bittig et al., 2018). Response time corrections have been applied to surface measurement systems using membrane-based sensors (Canning et al., 2020) and traditional equilibrators (Kodovska et al., 2016; Pohlman et al., 2017). Similar corrections are not generally applied to analytic systems with rapid (1–2 minute) response times or those aiming for large scale concentration and sea-air flux patterns (e.g. Pfeil et al., 2013) because the effort and uncertainty associated with this procedure may not be justified. However, to capture small-scale spatial and temporal dynamics of CH4, which is less soluble and therefore takes longer to equilibrate than N2O (see Table 1), *τ* corrections can improve the resolution of surface concentration and sea-air flux mapping (e.g. Pohlman et al., 2017; Canning et al., 2020). A comprehensive description of the application of a *τ* correction for equilibrator-based and membrane-based systems is, nonetheless, beyond the scope of this SOP. Recent studies have addressed the application of optical sensors for mapping surface gas concentrations (Bittig et al. 2018; Canning et al. 2020), but a detailed study that compares the performance of passive-membrane, contact-membrane and equilibrium-based gas extraction systems is lacking. Such a study will require a parameterization that takes into account the short and long-term effects of the temperature, salinity, flow rates and turbidity of the incoming water, as well as the execution of concentration step experiments under field conditions.

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