Marine carbonyl sulfide (OCS) and carbon disulfide (CS$_2$): a compilation of measurements in seawater and the marine boundary layer

Sinikka T. Lennartz[1,*], Christa A. Marandino[1], Marc von Hobe[2], Meinrat O. Andreae[3,4], Kazushi Aranami[5], Elliot Atlas[6], Max Berkelhammer[7], Heinz Bingemer[8], Dennis Booge[1], Gregory Cutter[9], Pau Cortes[10], Stefanie Kremser[11], Cliff S. Law[12, 13], Andrew Marriner[12], Rafel Simó[10], Birgit Quack[1], Günther Uher[14], Huixiang Xie[15], Xiaobin Xu[16]

[1]GEOMAR Helmholtz-Centre for Ocean Research Kiel, Marine Biogeochemistry, Düsternbrooker Weg 20, 24105 Kiel,
[*]now at: University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment, Marine Geochemistry, Carl-von-Ossietzky-Straße 9-11, Oldenburg
[2]Forschungszentrum Jülich GmbH, IEK-7, Jülich, Germany
[3] Max Planck Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany
[4]Scripps Institution of Oceanography, University of California San Diego,La Jolla, CA 92093-0230, USA
[5]Hokkaido University, Japan
[6]University of Miami, Atmospheric Sciences, Miami, FL, USA
[7]University of Illinois at Chicago, Dept. of Earth and Environmental Sciences, Chicago, IL, USA
[8]Goethe-University Frankfurt am Main, Institut für Atmosphäre und Umwelt, Frankfurt, Germany
[9]Old Dominion University, dept. Ocean, Earth & Atmospheric Sciences, Norfolk, VA, USA
[10]Institut de Ciències del Mar, Departament de Biologia Marina i Oceanografia, Barcelona, Spain
[11] Bodeker Scientific, Alexandra, New Zealand
[12]National Institute of Water and Atmospheric Research (NIWA), Wellington, New Zealand
[13]Department of Marine sciences, University of Otago, New Zealand[14] School of Natural and Environmental Science, Newcastle University, Newcastle upon Tyne, U. K.
[15] Institut des sciences de la mer de Rimouski, Université du Québec à Rimouski, Rimouski, Canada
[16] Key Laboratory for Atmospheric Chemistry of China Meteorology Administration, Chinese Academy of Meteorological Sciences, Zhongguancun Nandajie 46, Beijing 100081, China

Correspondence to: Sinikka T. Lennartz (sinikka.lennartz@uni-oldenburg.de)

Abstract. Carbonyl sulfide (OCS) and carbon disulfide (CS$_2$) are volatile sulfur gases that are naturally formed in seawater and exchanged with the atmosphere. OCS is the most abundant sulfur gas in the atmosphere, and CS$_2$ is its most important precursor. They have gained interest due to their direct (OCS) or indirect (CS$_2$ via oxidation to OCS) contribution to the stratospheric sulfate aerosol layer. Furthermore, OCS serves as a proxy to constrain terrestrial CO$_2$ uptake by vegetation. Oceanic emissions of both gases contribute a major part to their atmospheric concentration. Here we present a database of previously published and unpublished, mainly ship-borne measurements in seawater and the marine boundary layer for both gases, available at https://doi.pangaea.de/10.1594/PANGAEA.905430 (Lennartz et al., 2019). The database contains

original measurements as well as data digitalized from figures in publications from 42 measurement campaigns, i.e. cruises or time series stations, ranging from 1982 to 2019. OCS data cover all ocean basins except for the Arctic Ocean, as well as all months of the year, while the CS_2 dataset shows large gaps in spatial and temporal coverage. Concentrations are consistent across different sampling and analysis techniques for OCS. The database is intended to support the identification of global spatial and temporal patterns and to facilitate the evaluation of model simulations.

1 Introduction

Carbonyl sulfide (OCS) is the most abundant sulfur gas in the atmosphere with a tropospheric mixing ratio around 500 ppt (Kremser et al., 2016). Carbon disulfide (CS_2) is a short-lived sulfur gas, which is oxidized within hours to days. Because OCS is a major product of this oxidation with a yield of 82 % (i.e. 82 molecules of OCS produced from 100 CS_2 molecules), CS_2

10 oxidation is a major source of OCS in the atmosphere.

Atmospheric mixing ratios of OCS show larger annual than interannual variations (Montzka et al., 2007). Small negative trends between 10-16% decrease derived from firn air and flask measurements have been reported for the 1980 to 2000 period (Montzka et al., 2004). Since 2001, small positive trends <10% per decade were derived from OCS observations in the Southern hemisphere (Kremser et al., 2015).

15 Due to its long tropospheric lifetime of 2-7 years, OCS is entrained into the stratosphere. In volcanically quiescent periods, OCS (and indirectly CS_2) is thought to be a major contributor to stratospheric sulfate aerosols that influence the radiative budget of the Earth (Crutzen, 1976; Brühl et al., 2012). In addition, OCS can be used as a proxy to quantify the CO_2 uptake of plants (gross primary production), which is a major source of uncertainty in climate modelling (Whelan et al., 2018). Both scientific interests benefit from a well constrained atmospheric budget. OCS and CS_2 are produced naturally in the ocean, and

20 their oceanic emissions contribute substantially to their atmospheric concentrations (Chin and Davis, 1993; Watts, 2000; Kremser et al., 2015).

Oceanic source estimates of OCS and its precursor CS_2 still contain large uncertainties (Kremser et al., 2016; Whelan et al., 2018). Current efforts to model surface concentrations of OCS in seawater diverge in their results (Launois et al., 2015; Lennartz et al., 2017). Most measurements on oceanic OCS and CS_2 were performed in the 1980s and 1990s, and data are

25 often not available or stored inaccessibly for use, hampering model evaluation or analysis of global spatial and temporal concentration patterns. Therefore, a combined database for marine measurements of OCS and CS_2 has been given high priority in a recent review on using OCS as a tracer for gross primary production (Whelan et al. 2018). Here, we aim to provide such a comprehensive database by compiling previously reported as well as unpublished data, from corresponding authors of the original studies or via digitalization from pdf documents.

30 Both OCS and CS_2 show a pronounced variability in seawater which implies a need for highly resolved observations. Therefore, we pay special attention to the temporal resolution of measurements in the database. The seasonal variability is a direct result of the marine cycling of both gases. Photochemical reactions involving chromophoric dissolved organic matter

(CDOM) lead to the formation of OCS, as does a light-independent production pathway (Ferek and Andreae, 1984; Weiss et al., 1995a; Von Hobe et al., 2001). OCS is efficiently hydrolyzed in seawater. The temperature dependence of the hydrolysis reaction leads to high degradation rates in warm waters (Elliott et al., 1989; Radford-Knoery and Cutter, 1994; Kamyshny et al., 2003). The efficient photochemical production, as well as the fast degradation in warm waters result in strong diurnal and

5   seasonal cycles of OCS in the surface ocean (Kettle et al., 2001; Ulshöfer et al., 1995). CS_2 is photochemically produced in seawater as well, but diurnal cycles are not as pronounced due to lower efficiency of the sink processes. Concentrations of CS_2 and OCS in seawater differ strongly depending on the time of day and season measured. To facilitate interpretation of concentration measurements on larger scales in relation to the processes described above, ancillary data coinciding with trace gas measurements are also reported if available, such as meteorological or physical seawater properties. The database is

10   described with respect to number of data, range and patterns of concentrations, analytical methods, temporal and spatial coverage and sampling frequency for each dataset.

2 Methods

2.1 Data collection

Data were obtained either from authors of previous studies directly or digitalized with a web based digitalization tool from pdf

15   documents. Web of Science was searched for the key words 'carbonyl sulfide' (both sulfide and sulphide), 'carbon disulfide' (both sulfide and sulphide) in connection with 'ocean' or 'seawater'. When data could not be obtained directly from authors, relevant figures were identified and digitalized with the WebPlotDigitizer Automeris (URL: https://apps.automeris.io/wpd/, accessed January 2019). When digitalizing the data from documents, concentration data were rounded to the integer to account for uncertainty in the digitalization method introduced, e.g., by misalignment of the axes in case of old, scanned pdf documents.

20   We include here only shipborne measurements or observations from stations with a marine signal (i.e. research platform in the North Sea ID15, Amsterdam Island ID6, Bermuda ID39). For atmospheric OCS data from aircraft campaigns or continental time series stations, i.e. HIAPER-Pole-to-Pole-Observations (HIPPO, Montzka (2013)), Atmospheric Tomography Mission (ATom, Wofsy et al. (2018)) as well as the NOAA time series stations from the Earth System Research Laboratory – Global Monitoring Division (NOAA-ESRL, Montzka (2004), Montzka et al. (2007)) we refer to the respective repositories accessible

25   online (HIPPO: https://www.eol.ucar.edu/field_projects/hippo; ATom: https://espo.nasa.gov /atom/content/ATom, NOAA-ESRL: https://www.esrl.noaa.gov/gmd/).

Concentration data were converted to the unit picomole OCS/CS_2 per liter, accounting for molar masses of sulfur (32.1 g), OCS (60 g) and CS_2 (76.1 g). Data were collected together with the following metadata (if reported in the original publication or otherwise available):

30   -   Latitude of measurement
        -   Longitude of measurement
        -   Date, including year, month, day, hour, minute

- Name of the cruise and/or ship
- Contributor
- Main reference for data
- Method description
5 - Main reference for method
- Sample depth
- Any ancillary data (meteorological, physical, biological data)
- Flag describing the sampling resolution (see Tab. 1).

It should to be noted that several commonly used materials such as any rubber parts may lead to contaminations when
10 measuring OCS and CS_2. A non-exhaustive list of problematic materials is available here http://www.cosanova.org/materials-to-avoid.html (accessed February, 2019). We paid attention to the method description of each dataset, and data were only included when blank measurements are reported or the description of the material was provided (e.g. Teflon used). An overview of the dataset is provided in Tab. 2 (methods) and Tab. 3 (sampling details). A filling value of -999 was introduced for concentrations below the respective detection limit of each individual dataset. Missing additional data (physicochemical
15 parameters, meteorological parameters etc.) was filled with NaN (not a number), to facilitate readability in data handling software. The database can be accessed at the data repository PANGAEA (https://doi.pangaea.de/10.1594/PANGAEA.905430, (Lennartz et al., 2019). Available additional data is listed in Tab. 4.

2.2 Trace gas analysis

20 **2.2.1 Carbonyl sulfide in seawater**

Carbonyl sulfide (OCS) concentrations in seawater were commonly measured with a method to separate gaseous OCS from the seawater, connected to a detection system. Two main principles were applied to separate OCS from seawater: 1) purging the water sample with an OCS-free gas to transfer the total dissolved OCS into the gas phase, or 2) using an equilibrator, where a gas phase is brought into equilibrium with the seawater sample. The OCS concentration in water is then calculated using
25 Henry's law and the temperature during the equilibration process. Sampling using method 1 is usually performed discretely, and has sometimes been replaced by method 2 with automated (semi-)continuous sampling with a sampling resolution of <15 minutes since 2015 (Ulshöfer et al., 1995; Von Hobe et al., 2008; Lennartz et al., 2017). OCS detection in discrete samples used gas chromatography (GC). Most GCs were then coupled to a flame photometric detector (GC-FPD), or, less frequently, to an electron capture detector (GC-ECD). Commonly, samples were cryogenically pre-concentrated (e.g. with liquid N_2) prior
30 to injection into the GC. A new technique using off-axis integrated cavity output spectroscopy (OA-ICOS) has only recently been developed to continuously measure dissolved OCS in seawater with the use of an equilibrator (Lennartz et al., 2017).
For the majority of the samples in the database, the precision was reported to be better than 10%, and the limit of detection is around 2 pmol L^{-1} (see Tab. 2 for details on individual datasets). The instability of OCS in water makes the comparison with

liquid standards difficult, which is why most of the studies used permeation tubes to calibrate their instruments. Unfortunately, no inter-calibration between cruises is reported (see section 3.1 for a discussion of quality control of the data).

2.2.2 Carbonyl sulfide in the marine boundary layer

Quantifying the OCS concentration in the sampled gas is performed in a similar way, with the same analytical systems, as described in section 2.2.1 for dissolved concentration measurements. The database consists mainly of shipborne measurements, but includes measurements from two land-based stations with strong marine influence. These two datasets are (1) ID6 from Amsterdam Island in the Southern Ocean, and (2) ID39 from Tudor Hill, Bermuda.

The majority of studies used a GC-FPD system; GC-ECD and OA-ICOS were less frequently used. Detection limits and precision was comparable or identical to seawater measurements described in the previous section. Details on each individual method are listed in Tab. 2. Quantification was achieved with standards produced from permeation tubes and from gas cylinders from various manufacturers (see Tab. 2 for specifications of individual studies). No inter-calibration for the complete database is available.

2.2.3 Carbon disulfide in seawater

Sampling of carbon disulfide (CS_2) was performed discretely from both continuously pumped water and from containers such as Niskin bottles. Concentrations of CS_2 were measured with a sampling frequency of up to 15 minutes. Most frequently, a GC-MS system was used; GC-FPD was less common. Prior to the injection in the GC, samples were either purged with CS_2-free gas, and a cooled trap was used for preconcentration (purge+trap system), or the gas and liquid phase were brought to equilibrium with an equilibrator. Detection limits ranged down to 1 pmol L^{-1}, and the precision was around 3-5% (see Tab. 2 for specification of the individual datasets). Standard measurements include permeation tubes or liquid standards prepared in ethylene glycol, but no inter-calibration has been reported.

2.2.4 Carbon disulfide in the marine boundary layer

Samples were commonly taken discretely from the vessel's deck, directly into air canisters, or sampled directly from air drawn with tubing into the laboratory. Altitudes where samples were taken ranged from 10-25m. The detection of CS_2 in the gas phase was similar to the analytical methods described in the section 2.2.3, without the step of purging the gas out of the water. GC-MS or GC-FPD were used for detection. As described above, detection limits range down to 1 ppt, and the precision is ~3-5% (see Tab. 2 for specification of the individual datasets). Standards were either permeation tubes or gas cylinders, detailed in Tab. 2.

3 Description of dataset

All data sets included here provide some means of quality control, and calibration procedures including primary gravimetric standards from permeation tubes or by certified gas standards are described in the original publications. However, the database compiled here includes measurements made by different laboratories and, thus, different measurement systems. One limitation of the database is the missing intercalibration across these different measurement systems. Since many of these systems were built and deployed in the 1990s and do no longer exist, such an intercalibration is not possible anymore. We strongly recommend undertaking efforts for intercalibration across laboratories for future oceanic measurements of OCS and CS_2. Since no practical quality control is possible, we assess the quality of the database by its internal consistency.

3.1 Carbonyl sulfide in seawater

Measurements of OCS in seawater were collected from 32 cruises, resulting in 7536 individual measurements (Fig. 1, Tab. 2 and 3). OCS concentrations were measured in the picomolar range in the surface and subsurface ocean, with a mean concentration of 32.3 pmol L^{-1} (n=7536, Fig. 2a), ranging from below the detection limit to 1466 pmol L^{-1} in Rhode Island river estuary.

The majority of measurements were made in the Atlantic Ocean, least from the Indian Ocean. No measurements are available for the Arctic Sea. The sampling was heavily biased towards surface ocean measurements shallower than 10m depths, and only few measurements (<3%) were obtained from concentration profiles in the water column (144 measurements). The available profiles range down to a water depth of 2000m (Tab. 3). Reporting the sampling depth is critical for photochemically produced substances such as OCS, as the penetration depths of UV light and hence the photoproduction varies spatially and temporally. Samples that were obtained from depths shallower than 10m are referred to as 'surface samples', most of them were obtained at a depth of 3-5m. Maintaining a continuous water supply despite water level changes by waves on a moving vessel is a challenge and currently hinders continuous sampling at shallower depths. Profile measurements from the North Atlantic indicated that differences in concentration within the surface of the mixed layer <10m are in a range of about 5 pmol L^{-1} (Cutter et al., 2004), but might potentially become larger with surface stratification and high irradiation (Fischer et al., 2018).

OCS measurements were reported in 12 minutely to monthly resolution (Fig. 3e). Hence, the majority of the database has the required temporal resolution to cover the full range of the diurnal variation, i.e. a measurement interval of 4h or less is needed to minimize averaging errors due to interpolation.

The global variability of the available measurements shows lowest concentrations in tropical and subtropical waters, especially compared to concentrations at higher latitudes of the Southern hemisphere (Fig. 3a). The pattern of highest OCS concentrations in coastal and shelf regions has been reported for individual datasets (Cutter and Radford-Knoery, 1993), but is also recognizable in this global database. Especially the data from cruise ID10 (Cutter and Radford-Knoery, 1993), which covers estuaries and shelfs, is 10-1000 fold higher than in oligotrophic warm waters (Fig. 4a). This pattern is also evident in elevated

concentration in the North Sea (Uher and Andreae, 1997), the Mediterranean Sea (Ulshöfer et al., 1996) and the coastal waters of Amsterdam Island in the Indian Ocean (Mihalopoulos et al., 1992). Concentration profiles in the water column show a typical photochemical behaviour and decrease with depth, although subsurface peaks occur occasionally (Von Hobe et al., 1999; Cutter et al., 2004; Lennartz et al., 2017). Despite the still limited size of the database, it already covers a large part of the global variability, as it includes measurements from a variety of different biogeochemical regimes, i.e. from oligotrophic waters (Cutter et al., 2004; Lennartz et al., 2017; Von Hobe et al., 2001) to higher trophic stages in shelf (Uher and Andreae, 1997), estuary (Cutter and Radford-Knoery, 1993) and upwelling regions (Ferek and Andreae, 1983; Mihalopoulos et al., 1992; Von Hobe et al., 1999; Lennartz et al., 2017).

The annual pattern illustrated in Fig. 3c is different for the Southern and Northern hemisphere. Lowest median concentrations in the Southern hemisphere are present during austral winter months, and increase up to five times during austral summer. In the Northern hemisphere, lowest concentrations are present during late boreal summer (A,S,O) and late boreal winter (J,F,M). The range of observed concentrations is similar for both hemispheres. Compared to the spatial pattern in Fig. 3a, the seasonal variability in the database is larger than the spatial variability.

Figure 4a illustrates the concentration range of each dataset for OCS in seawater. The internal consistency of the database is supported by: (1) the variation of concentration in this database is consistent with the current process understanding, and thus reflects actual variability. The majority of the global measurements (60%) fall into a very narrow range of 8.7-43.0 pmol L^{-1}, and outliers of this 20-80 percentile range are explicable by location or time of measurement. For example, OCS concentrations during cruise ID2, ID10, ID13 and ID19 were much higher than observed by other cruises (Fig. 4), which can be explained by the location of Chesapeake Bay (ID2, ID13), the Petaquamscutt estuary (ID 10) and North Sea (ID19) in shelf areas or close to estuaries, where high CDOM abundance enhances photochemical production and increases concentration. An example for a particularly low concentration is cruise ID18, which took place during winter. The authors refer the low concentration as due to low photoproduction at that time (Ulshöfer et al., 1995); (2) Measurements obtained from cruises that cover a similar temporal and spatial area yield comparable results, such as cruises ID3 and ID4 (Pacific Ocean), cruises ID27 and ID28 (Atlantic transects) or cruises ID20, ID26, and ID32 from the North Atlantic (Fig. 4); (3) Reported OCS concentrations in seawater and the marine boundary layer are consistent across different laboratories and methods. The introduction of new methods, e.g. OA-ICOS (cruiseID 36 and 39) yields results that are comparable to previous measurements using GC-FPD. To facilitate comparison of individual datasets, they are grouped according to the analysis system used in Tab. 2 (capital letters in last table column).

3.2 Carbonyl sulfide in the marine boundary layer

The dataset of OCS in the marine boundary layer includes 14291 measurements from 30 cruises (Fig. 3f, Tab. 3). The average mixing ratio in the marine boundary layer is 548.9 (209-1112) ppt. All major ocean basins were covered, except for the Arctic Ocean. The North Atlantic Ocean including the North Sea was sampled most frequently.

Sampling of OCS in the marine boundary layer is done either discretely by pumping air in canisters, or continuously by pumping air directly into the detection system (see Tab. 2 for details). Marine boundary layer air was often sampled from the ship's uppermost deck, and reported sampling heights ranged from 10-35 m (Tab. 3). Given the relatively stable atmospheric mixing ratios (compared to the strong diel variations of dissolved OCS), a strong gradient in mixing ratios towards the sea surface is not expected. Hence, the database is suited to calculate the concentration gradient across the air-sea boundary, making it valuable for calculating oceanic emissions. The sampling frequency in individual datasets ranged from intervals shorter than hourly to monthly time series (Fig. 3f). Given the weak diurnal variability compared to the seasonal variability, the reported resolution in all of the individual datasets is sufficient for large scale comparisons.

The global variability of boundary layer OCS mixing ratio is less pronounced and does not show the same spatial pattern as that of dissolved OCS in the surface ocean (Fig. 2b). Ranges of mixing ratios are similar across all latitude bins, with minor variations (Fig. 3b). In several individual datasets, e.g. in Pacific (Weiss et al., 1995b) and Atlantic transects (Xu et al., 2001), mixing ratios in the tropics increase compared to higher latitudes during the respective cruise (Fig. 2b). Highest atmospheric mixing ratios are reported from around Europe (including the Mediterranean) as well as off the Falkland Islands (Fig. 2b). The complete database includes measurements from January to December in the Northern hemisphere, but data for September are missing in the Southern hemisphere. The seasonal variability in atmospheric mixing ratio was less pronounced compared to the variability in seawater OCS concentration, with monthly medians ranging from 439-647 ppt in the Northern and 467-523 ppt in the Southern hemisphere. No clear seasonal pattern was observed in either of the hemispheric datasets. The lack of such a pattern in atmospheric concentrations might result from the limited size of the dataset and the spatial heterogeneity of the sampling locations (i.e. influence of local vegetation sinks or anthropogenic sources of the air mass history). It should also be noted that small decadal trends as reported in the introduction could influence the reported differences, as the measurements reported here span a period of 1982-2018. Also, possible standardization and calibration issues could potentially be larger than the range of reported trends, so using the dataset in new trend studies should only be done with caution.

The internal consistency of the database is of similar quality as described for OCS in seawater. 60% of the data (i.e. between 20 and 80 percentile) fall in a narrow range of 477-621 ppt (Fig. 4b). Some features are present across different datasets and, hence, support the internal consistency of the dataset: For example, locally elevated mixing ratios in tropical latitudes are present in single datasets, and also globally (Fig. 2b and 4b). Elevated atmospheric mixing ratios were reported by several studies providing measurement from around Europe (Fig. 2b and 4b).

3.3 Carbon disulfide in seawater

Measurements of dissolved CS_2 in seawater are reported from 11 cruises (Fig. 1, 1813 measurements), with an average of 15.7 (1.1-376) pmol L^{-1}. Most of the measurements were performed in the Atlantic Ocean, comprising three Atlantic meridional transects (Fig. 2c). No measurements are available from the Arctic and Antarctic waters and the Indian Ocean.

The latitudinal variation of CS_2 in seawater was small (Fig. 5a, on average <5 pmol L^{-1}), although individual studies report a general covariation of concentrations and water temperature (Xie and Moore, 1999; Lennartz et al., 2017). Apart from an

Atlantic transect with exceptionally high concentrations (Lennartz et al., 2017), concentrations tend to increase towards coastal and upwelling regions (Fig. 2c), but this increase was less pronounced compared to the spatial variability of OCS (Fig. 2a). Seasonal variability of CS_2 water concentrations was larger compared to the spatial variability (Fig. 5a and 5c), but did not show a clear seasonal or spatial pattern. Concentrations were comparable in the Northern and Southern hemisphere. Diurnal variability of surface concentrations was present on some, but not all days within individual datasets, likely representing the varying efficiency of the local sink process in the mixed layer. The occurrence of diel cycles calls for a similarly high sampling frequency as suggested for OCS (i.e. more frequently than 4 hourly). However, most of the dataset comprises a sampling frequency of daily to monthly, and the sampling is biased towards daytime (Fig. 5e). Hence, averaged concentrations might slightly overestimate diel averages.

The database presented here indicates the common range of seawater concentrations and covers several biogeochemical regimes. However, limitations remain, viz.: 1) a general sparsity of measurements, 2) data gaps especially in high latitudes and 3) insufficient sampling frequency to cover full diel variability in many individual data sets.

The limited size of the database for CS_2 in seawater hampers internal data comparison. The majority of the data (between 20 and 80 percentile) falls in the range of 6.1-15.6 pmol L^{-1}. Individual datasets from the Southern Ocean (cruiseID 7, not georeferenced) and from an Atlantic transect (cruiseID 38) show mean concentrations that are considerably higher than observed on other cruises (Fig. 6a). Since data from datset ID7 represent the only available measurements for this location, based on this database, we cannot determine whether this is an artefact or not. However, we see a similar trend in the OCS data observed by dataset ID7. Also, the low atmospheric mixing ratio measured during this specific cruise speaks against a contamination problem. For the Atlantic transect it is evident that the average concentration is higher compared to the other three Atlantic cruises with a similar cruise track, i.e. dataset ID28, ID29 and ID33. However, the minimum measured concentration in this specific dataset is 7 pmol L^{-1}, which makes a strong contamination unlikely. The atmospheric mixing ratios during cruise ID38 are also lower than those during the other two Atlantic transects, which negates a strong contamination problem. Furthermore, the covariance with temperature is evident in this and in other datasets (Xie and Moore, 1999; Lennartz et al., 2017). CS_2 concentration in dataset ID38 is reported twice daily, one time at 8-10 a.m. and one time at 15-18 a.m. local time. Potentially, the average is misleading in this respect, because it masks potential diel cycles. Daily maxima of cruise ID38 agree with daily maxima of some parts of the other Atlantic transects (ID28,29,33), but not on the majority of days. The minimum values over large parts of the cruise ID38 were higher than those in the cruises ID28, 29 and 33. Potentially, the minima might have been missed by the coarse sampling.

3.2 Carbon disulfide in the marine boundary layer

CS_2 measurements in the marine boundary layer are only available for the Atlantic Ocean from six cruises, i.e. 1036 individual measurements. Atmospheric mixing ratios were on average 42.2 ppt (2.5 to 275.7 ppt, Fig. 2d).

The reported CS2 concentrations are generally higher than those reported from airborne measurements in previous studies, where values <10 ppt in the boundary layer have been reported (Cooper and Saltzman, 1993). An influence of continental air carrying a higher concentration of CS_2 might be a possible explanation for elevated values (see e.g. compilation in Khan et al. (2017) of up to 1200 ppt). The short atmospheric lifetime of CS_2 sets a limit to long range transport, so this explanation would only hold for coastal and shelf regions. The data reported here have undergone calibration procedures as reported in the original manuscripts and elevated values are consistent across different labs and locations, so contamination problem of the local measurement systems are unlikely but cannot be ruled out completely to be responsible for the elevated mixing ratios.

Since this dataset is only comprised of four individual cruises, any perceived pattern in global variation should be taken with caution, as it might rather reflect natural variability or differences between individual laboratories. Spatiotemporal variability will become clearer once more data are available. Almost no preference is given to new measurement locations or times, as any new dataset will help to further constrain spatial and temporal variability of CS_2 concentration. Latitudinal median mixing ratios varied between studies by a factor of 2, but due to the limited size of the dataset, it is currently unclear if this variation is meaningful. However, a CS_2 mixing ratio of 42.2 ppt in the marine boundary layer may become relevant for calculation of oceanic emissions. Commonly, marine boundary layer concentrations of CS_2 are assumed to be 0 due to its short lifetime, which will lead to an overestimation of emissions in case the true mixing ratio is higher, as our database indicates (at a temperature of 20°C, a salinity of 35 psu, a wind speed of 7 m s^{-1} and a CS_2 water concentration of 16 pmol L^{-1}, the difference between 0 and 42 ppt CS_2 in air leads to an overestimation of 21%).

Due to the sparsity of data and the expected strong variability resulting from the short atmospheric lifetime, we will not use this limited dataset here for assessing the internal consistency across locations. The variation between the two Atlantic transect datasets ID28 and ID29 with a strong overlap in measured mixing ratios seems reasonable (Fig. 6b), but more data is needed to establish a comparison on larger scale.

4 Recommendations for oceanic OCS and CS_2 measurements

The full potential of an oceanic OCS and CS_2 database can be exploited, if measured concentrations are stored together with relevant metadata. As a minimal requirement, we recommend to report i) the exact date of each measurement, including time of the day and ii) the exact location (including latitude, longitude and sample depth). This is especially important due to the photochemical production of both gases, as concentration in seawater varies strongly on diurnal and seasonal scales. To obtain a full diurnal cycle, we recommend to measure at least in a 4-hr-resolution, to minimize errors when interpolating and averaging over the period of one day. Of secondary importance are physical parameters such as temperature, radiation and wind speed. When modelling marine concentrations of OCS and CS_2, it is helpful to have access to the CDOM absorbance data at a wavelength of 350 nm, because parameterizations for production rates are based on this value (von Hobe et al., 2003; Lennartz

et al., 2017). In order to decipher the history of the air mass and identify potential continental influence, it would also be helpful to measure additional trace gases such as CO or other anthropogenic tracers simultaneously.

In order enable the identification of large scale patterns and the quantification of the oceanic source strength, we identify locations for future measurements. For OCS seawater concentration, large gaps exist in the open Pacific Ocean and the Arctic Ocean. The Arctic Ocean would be especially interesting due to the unique composition of dissolved organic matter derived from river input, which could influence OCS production in the water. Marine boundary layer OCS is required especially from the Arctic Ocean. The data coverage for CS_2 is very scarce, but especially measurements in water and marine boundary layer from high latitudes (Southern Ocean and Arctic Ocean) as well as Indian Ocean and Southern Pacific would be helpful. Generally, for both gases, water concentration profiles would be helpful to understand their processes in the subsurface. This is important for CS_2 which has a long lifetime in water, so that mixing processes could bring subsurface CS_2 in contact with the atmosphere. Similarly, repeated measurements from the same locations would be helpful to decipher any trends.

5 Data availability

The data is available from the PANGEA database (https://doi.pangaea.de/10.1594/PANGAEA.905430, (Lennartz et al., 2019) .

6 Competing interests

The authors declare no competing interests.

Author contributions

S.T.L. and C.A.M. started the initiative for data compilation and long-term storage. All coauthors contributed data from one or more expeditions. S.T.L. wrote the manuscript with input from all coauthors.

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Tables

Table 1. Flags used to describe sampling frequency of each individual dataset.

0	not reported
1	minutely
2	15-minutely
3	hourly
4	1-4 hourly
5	>4 hourly to daily
6	monthly
7	seasonally
8	annually
9	irregular

Table 2. Description of all cruises or campaigns contributing measurements to this database. Cruises are given a unique ID for identification. Reference refers to the publication where the data was reported first. Methods are reported using the same specifications and level of detail as given in the original publication. Specifications for analytical methods are listed together with the method referenced in the main reference. di/or stands for digitalized/original data. S=sampling, An=analysis, Det=details, R=reference of instrumentation. Letters in the last column indicate direct comparability of the datasets, as studies were performed with either identical analytical systems (i.e. same method reference), or performed by the same laboratory through further development of analytical systems (i.e. different method reference, but intercomparison within laboratory).

ID	campaign/ship/ date/region	reference	method	data	grouping
1	RV Robert Conrad June 1982 ETSP	Ferek and Andreae (1983)	OCS S: gas bubbler in glass column An: GC-FPD Det: precision <10%, st. dev. of triplicates 6% R: Ferek and Andreae (1983),	di	A
2	RV Cape Hatteras April 1983 Chesapeake Bay	Ferek and Andreae (1984)	OCS S: gas bubbler in glass column An: GC-FPD R: Ferek and Andreae (1983)	di	A
3	RV Discoverer March-June 1982	Johnson and Harrison (1986)	OCS S: glass syringes/ bucket	di	B

	Pacific		An: GC-FPD Det: standard from permeation tubes, l.o.d. 0.04 ngS, reproducibility within 2.5%, not georeferenced R: Johnson (1985)		
4	RV Discoverer March-June 1983 Pacific	Johnson and Harrison (1986)	OCS S: glass syringes/ bucket An: GC-FPD Det: standard from permeation tubes, l.o.d. 0.04 ngS, reproducibility within 2.5%, not georeferenced R: Johnson (1985)	di	B
5	RV Columbus Iselin April-May 1986 Atlantic	Kim and Andreae (1992)	CS_2 S: purged with N_2 An: GC-FPD Det: liquid CS_2 standard cross checked with gas standard Metronic Associates Inc.(Santa Clara, CA), precision 9%, l.o.d. 2 pmol S L^{-1} R: Kim and Andreae (1987)	di	C
6	Coastal 1987-1888 Amsterdam Island, Indian Ocean	Mihalopoulos et al. (1991)	OCS S: pressurized electropolished stainless steel canisters An:GC-FPD/FPD Det: standard: gas standard Matheson Union Carbide, l.o.d. 0.4 ng OCS = 53 ppt, reproducibility <5% (8 repeats), accuracy 10%, not fully georeferenced R: Belviso et al. (1987)	di	D
7	RV Polarstern 1988 Atlantic, Southern Ocean	Staubes et al. (1990)	OCS, CS_2 S: purged with N_2 An: GC-FPD Det l.o.d. 3-4pptv and 0.5-1 ngS L^{-1}, not georeferenced R: Staubes et al. (1990)	di	E
8	RV Cape Hatteras April 1989 North Atlantic	Radford-Knoery and Cutter (1994)	OCS S: sampling with Go-Flo bottles, acidified, stripped with He An: GC-FPD Det: l.o.d. 1.3 pmol L^{-1}, precision 5% R: Cutter and Radford-Knoery (1993)	di	F
9	RV Cape Hatteras November 1989 Estuary, North Atlantic	Radford-Knoery and Cutter (1994)	OCS S: sampling with Go-Flo bottles, acidified, stripped with He An: GC-FPD Det: l.o.d. 1.3 pmol L^{-1}, precision 5% R: Cutter and Radford-Knoery (1993)	di	F
10	RV Cape Henlopen June 1990 North Atlantic	Cutter and Radford-Knoery (1993)	OCS S: Go-Flo bottles, gas-tight syringes, stripped with He An: GC-FPD Det: l.o.d. 1,3 pmol/L, precision 5%, R: Cutter and Radford-Knoery (1993)	di	F

11	RV Polarstern November 1990 Southern Ocean	Staubes and Georgii (1993)	OCS S: air: directly to sample loop, water: into gas stripping column with N_2 An: GC-FPD Det: l.o.d. 3.5ppt, 6.4% precision R: Staubes et al. (1989)	di	E
12	OCEAT II+III, diverse 1987-1991 Mediterranean Sea, Red Sea, Indian Ocean	Mihalopoulos et al. (1992)	OCS S: pressurized electropolished stainless steel canisters An: GC-FPD Det: lod: 0.4 ng S, precision 10%, not georeferenced R: Mihalopoulos et al. (1992)	di	D
13	Chesapeake Bay time series 1991-1994 Chesapeake Bay	Zhang et al. (1998)	OCS S: depth profiles with pump, Go-Flo, cubitainer, stripped with He An: GC-FPD C: standard: permeation tubes, precision <5%, l.o.d. 10 pmol OCS L^{-1} R: Cutter and Radford-Knoery (1993)	dii	F
14	RV Meteor – M21 April 1992 North Atlantic, North Sea	Ulshöfer et al. (1995)	OCS S: equilibrator An: GC-FPD Det: standard: permeation tubes, l.o.d. OCS: 100ppt, reproducibility 15% R: Uher (1994)	or	G
15	FP Nordsee September 1992 North Sea	Uher and Andreae (1997)	OCS S: equilibrator An: GC-FPD Det: standard: permeation tubes, l.o.d. 100 pg OCS=105ppt, precision <15% R: Ulshöfer et al. (1995), (Uher, 1994)	or	G
16	RV Aegaio, EGAMES July 1993 Mediterranean Sea	Ulshöfer et al. (1996)	OCS S: equilibrator An: GC-FPD Det: standard: permeation tubes, detection limit OCS: 4 pmol L^{-1}, precision 15% R: Uher (1994)	or	G
17	RV Surveyor November 1993 Pacific	Weiss et al. (1995b)	OCS S: glass syringe, purge-and-trap An: GC-ECD Det: standard: permeation tubes, l.o.d. 115 ppt cruise1, 23ppt cruise 2, uncertainty 6-10%, reproducability of blanks 7% R: Weiss et al. (1995a)	di	B
18	RV Meteor – M27 January 1994 North Atlantic, North Sea	Ulshöfer et al. (1995)	OCS S: equilibrator An: GC-FPD Det: standard: permeation tubes, l.o.d. OCS: 100 ppt, reproducibility 10% R: Uher (1994)	or	G
19	RV Valdivia April 1994	Ulshöfer and Andreae (1998)	OCS S:Weiss-type equilibrator	or r	G

	North Sea		An: GC-FPD Det: standard from permeation tubes, precision <10% R: Ulshöfer et al. (1995), (Uher, 1994)		
20	RV Columbus Iselin August 1994 North Atlantic (Florida)	Ulshöfer and Andreae (1998)	OCS S: Weiss-type equilibrator An: GC-FPD Det: standard from permeation tubes, precision <10% R: Ulshöfer et al. (1995) , (Uher, 1994)	or	G
21	RV Meteor – M30 September 1994 North Atlantic, North Sea	Ulshöfer et al. (1995)	OCS S: equilibrator An: GC-FPD Det: standard: permeation tubes, l.o.d. 100ppt, reproducibility <10% R: Ulshöfer et al. (1995)	or	G
22	RV Cape Hatteras March 1995 North Atlantic, Bermuda	Ulshöfer and Andreae (1998)	OCS S:Weiss-type equilibrator An: GC-FPD Det: standard from permeation tubes, precision <10% R:Ulshöfer et al. (1995)	or	G
23	RV Hudson July 1995 Atlantic, Pacific	Xie and Moore (1999)	CS_2 S: bucket/submersible pump An: GC-MS Det: gravimetrically prepared liquid standard, l.o.d. CS_2 1.5 pmol L^{-1} S, rel.st.dev. 1.4% at 10 pmol L^{-1} level R: Moore and Webb (1996)	or	H
24	RV Discoverer October 1995 Atlantic, Pacific	Xie and Moore (1999)	CS_2 S: stainless-steel Knudsen bottles An: GC-MS Det: gravimetrically prepared liquid standard, l.o.d. CS_2 1.5 pmol L^{-1} S, rel.st.dev. 1.4% at 10 pmol L^{-1} level R: Moore and Webb (1996)	or	H
25	RV Shirase November 1996 Indian Ocean, Southern Ocean	Inomata et al. (2006)	OCS S: PTFE-tubing, Flek-sampler An: GC-FPD Det: standard gas (Nippon Sanso Co. Ltd.), l.o.d. 0.06nmol L^{-1}/12ppt, uncertainty 6% R: Inomata et al. (1999)	di	I
26	RV Prof. Vodyanitsky, ACE-2 June 1997 North Atlantic	Von Hobe et al. (1999)	OCS S: Weiss-equilibrator An: GC-FPD, Det: standard: permeation tubes, l.o.d. 30ppt/0.4 pmol/L, precision <10% R: Von Hobe et al. (1999)	or	G
27	KH97-2 Jul 1997 North Pacific	Aranami (2004)	OCS, CS_2 S: Tedlar-bags An: GC-FPD Det: gas cylinder standard: Takachiho Kogyo Co. Ltd., precision 5%	or	J

			R: Aranami (2004)		
28	RV Polarstern ANTXV-1 November 1997 Atlantic transect	Xu et al. (2001)	OCS, CS_2 S: equilibrator An: GC-FPD Det: standard: permeation tubes, precision 3%, uncertainty 10% R: Xu et al. (2001)	or	K
29	RV Polarstern ANTXV-5 May 1998 Atlantic transect	Xu et al. (2001)	OCS, CS_2 S: Teflon-equilibrator An: GC-FPD Det: standard: permeation tubes, precision 3%, uncertainty 10% R: Xu et al. (2001)	or	K
30	RV Mirai MR98-K01 Nov. 1998 North Pacific	Aranami (2004)	OCS, CS_2 S: air: Tedlar-bags, seawater: plastic bucket, glass syringe An: GC-FPD Det: gas cylinder standard: Takachiho Kogyo Co. Ltd., precision 5% R: Aranami (2004)	or	J
31	RV Endeavor 327 April 1999 North Atlantic, BATS	Von Hobe et al. (2001)	OCS S:equilibrator An: GC-FPD Det: precision <2%, standard from permeation tubes, lod: 30 ppt/0.4pmol OCS R: von Hobe et al. (2000)	or	G
32	BATS August 1999 North Atlantic, BATS	Cutter et al. (2004)	OCS S: Go-Flo bottles, submersible pumping system An: GC-FPD Det: l.o.d. 1 pmol L^{-1}, precision <10% R: Radford-Knoery and Cutter (1994)	or	F
33	RV James Clark Ross, AMT-7 September 1999 Atlantic	Kettle et al. (2001)	OCS, CS_2 S: equilibrator An: GC-FPD C: permeation tubes R: Ulshöfer et al. (1995)	di	G
34	RV Poseidon P269 February 2001 Atlantic Ocean	partially published in Von Hobe et al. (2008)	OCS, CS_2 S:equilibrator An: GC-FPD Det: precision 1.9 % for COS and 2.2 % for CS_2, standard from permeation tubes, lod: 20 ppt/0.3pmol OCS and 10 ppt CS_2 R: Von Hobe et al. (2008)	or	G
35	RV Sonne, SHIVA November 2011 Pacific, Indian Ocean	unpublished	OCS S: gas canister An: GC-MS Det: referenced to NOAA standard, precision 1%, calibration accuracy 10% R: de Gouw et al. (2009)	or	L
36	RV Sonne, SPACES-OASIS July 2014 Indian Ocean	Lennartz et al. (2017)	OCS S: equilibrator An: OA-ICOS	or	M

			Det: standard permeation tubes, 15ppt precision, l.o.d. 4pmol/L =~200ppt standard within 2% of NOAA scale R: Lennartz et al. (2017)		
37	RV Atlantic Explorer Septermber 2014 North Atlantic, BATS	Berkelhammer et al. (2016)	OCS S: air via tube to instrument An: OA-ICOS Det: referenced against NOAA standard, std. dev. 12.7 ppt R: Berkelhammer et al. (2016)	or	N
38	RV Hesperides, TransPEGASO October 2014 Atlantic	Lennartz et al. (2017)	OCS, CS_2 S: glass bottles An: GC-MS Det: standards: gas (OCS), liquid (CS_2), l.o.d. OCS: 1.8 pmol L^{-1}, CS_2: 1.4 pmol L^{-1}, precision ~5% R:Lennartz et al. (2017)	or	O
39	Tudor Hill Observatory Dec 2014-Mar 2015 Bermuda	Berkelhammer et al. (2016)	OCS S: air via tube to instrument An: OA-ICOS Det: referenced against NOAA standard, std. dev. 12.7 ppt R: Berkelhammer et al. (2016)	or	N
40	RV Sonne, ASTRA-OMZ August 2015 ETSP	Lennartz et al. (2017)	OCS, CS_2 S: OCS: equilibrator, CS_2: Niskin bottles An: OCS: OA-ICOS, CS_2: GC-MS Det: OCS standard permeation tubes, 15ppt precision, l.o.d. 4pmol/L =~200ppt, standard within 2% of NOAA scale, CS_2: l.o.d. 1 pmol L^{-1}, precision 5-10% R: Lennartz et al. (2017)	or	M
41	RV Tangaroa Feb-Mar 2018 Southern Ocean	unpublished	OCS S: equilibrator An: OA-ICOS Det: standard permeation tubes, 15ppt precision, l.o.d. 4pmol/L =~200ppt R:Lennartz et al. (2017)	or	M
42	RV Xue Long Nov 2018 – Mar 2019 Pacific, Southern Ocean	unpublished	OCS S: Spray-head equilibrator An: OA-ICOS Det: standard permeation tubes, accuracy <18%, l.o.d. 4 pmol/L R: Lennartz et al. (2017)	or	M

Table 3: Quantitative sampling details for each individual dataset. #=number of samples, depth/height = water depth below sea surface, height above sea surface, t.r.=flag for temporal resolution, see Tab. 1. mbl=marine boundary layer, t.d.= top deck (height not specified).

ID	OCS seawater			OCS mbl			CS$_2$ seawater			CS$_2$ mbl		
	#	depth [m]	t.r.	#	height [m]	t.r.	#	depth [m]	t.r.	#	height [m]	t.r.
1	13	4	5									
2	18	1-18	5									
3	33	5	9	46	10	9						
4	115	5	9	101	10	9						
5							61	0-302	9			
6				8	25	0						
7	62		5	62	21	5	61	surface	5	58	21	5
8	18	16-850	5									
9	33	2-995	5									
10	5	3	5									
11	124	2	5	99	21	0						
12	109	diverse	0/6									
13	104	0-18	9									
14	118	3	3	118	28	3						
15	69	5	4	69	38	4						
16	123	3	4	123	6	4						
17				43		0						
18	120	7	4	120	38	4						
19	168	4	3	168	t.d.	3						
20	50	4	3	50	t.d.	3						
21	235	7	3	235	30	3						
22	323	4	3	323	t.d.	3						
23							17	surface	6			
24							17	surface	6			
25				12		5						
26	940	2-5	2	4175	10	2						
27				50	5	9				72		9
28	306	5	3	306	25	3	306	5	3	306	25	3
29	440	5	3	441	10-15	3	440	5	3	440	10-15	3
30	46	0-40	9	65	5	9	45		9	65	5	9
31	518		2	167		3						
32	132	1-300	4									
33	345	6	9	192		9	235	6	9			
34	287	1	2	95		3	287		2	95		3
35				193		4						
36	206	5	3	210	35	3						
37				1930		2						

38	42	5	5				42		5			
39				2213	23	3*						
40	285	5	3	256	35	3	144	5	3			
41	421		3	527		3						
42	1727	6	3	1908	t.d.	3						

*original paper in sampling frequency of seconds, averaged for this database

Table 4: Ancillary information available for the individual datasets. Physicochemical and meteorological data (water temperature, salinity, relative humidity, atmospheric pressure at sea level, wind speed, absolute wind direction, dew point temperature, chlorophyll a concentration, fluorescence, radiation, pH and precipitation) are directly included in the database. Availability of other trace gas measurements indicated, but the data is not included in the database . (others, available upon request).

Cruise ID	water temp.	salinity	rel.hum.	atm. pressure	air temp.	wind speed	wind direction	dew point	chlorophyll a	fluorescence	radiation	pH	precipitation	other gases
1														
2														
3														
4														
5														
6														
7														
8														
9														
10														
11														DMS
12														
13														
14	x	x	x		x			x						
15	x			x	x	x			x					
16														
17														
18	x	x	x	x	x	x		x						
19	x	x	x	x	x	x	x				x			
20	x	x	x	x	x	x					x			
21	x	x	x	x	x	x	x	x						
22	x	x	x	x		x	x			x	x			
23	x	x							x					
24	x	x							x					
25														DMS, H$_2$S
26	x	x	x		x	x	x		x			x	x	
27	x	x												DMS
28	x	x	x	x	x	x	x	x			x			
29	x	x	x	x	x	x	x	x			x			
30	x				x									DMS
31	x		x		x	x					x			
32														
33														DMS
34	x	x	x	x	x	x	x				x	x	x	
35														CO, others

36	X	X	X			X								CO, CO_2, others
37														CO, CO_2
38	X	X				X					X			DMS
39														CO, CO_2
40	X	X	X	X	X	X	X							CO, CO_2, others
41	X	X	X	X	X	X								CO, CO_2
42	X	X												CO, CO_2

Figures

Figure 1: Tracks of all cruises with OCS and/or CS$_2$ measurements included in the database (points depict stationary measurements).
5   **Labels indicate the cruise ID (compare Tab. 1).**
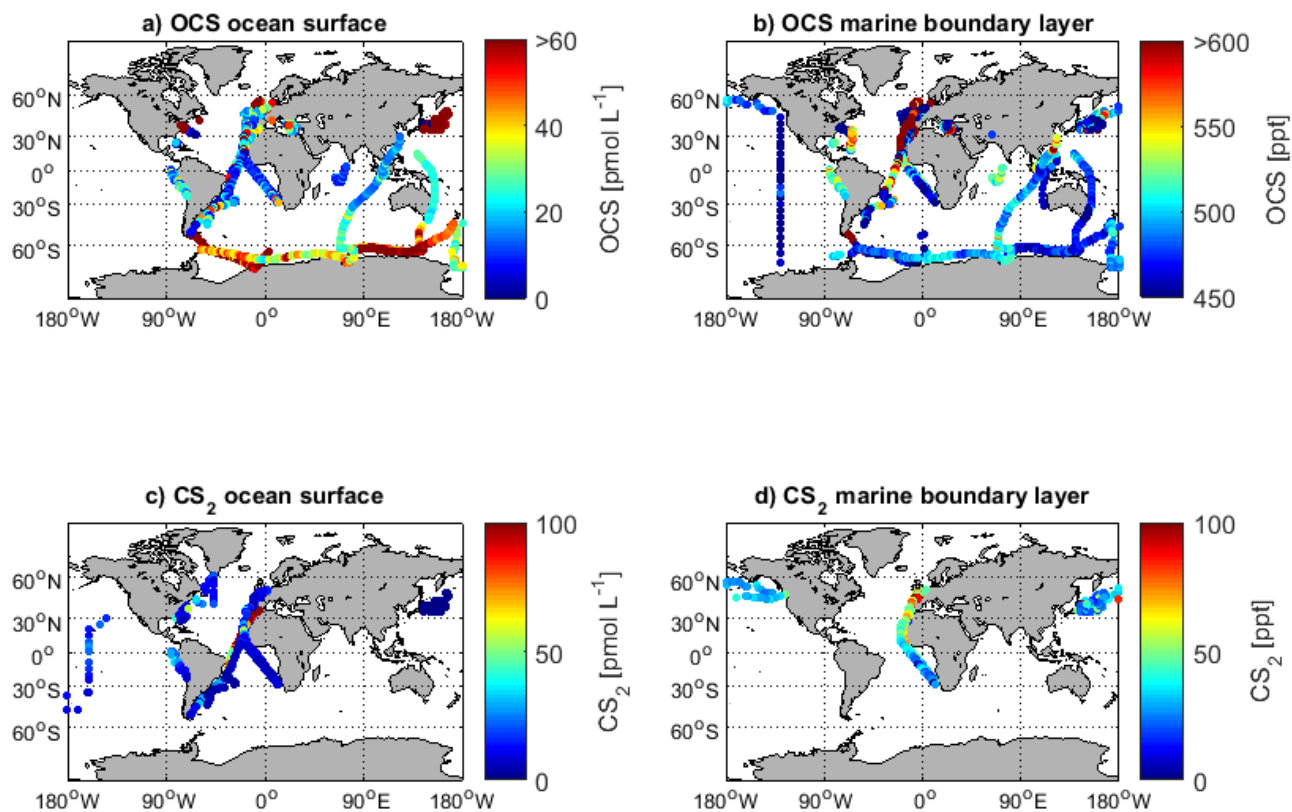
Figure 2: Georeferenced data for a) surface ocean OCS concentrations, b) marine boundary layer OCS mixing ratios, c) surface ocean CS₂ concentrations, d) marine boundary layer CS₂ mixing ratios. Only surface data (shallower than 10 m) are shown.
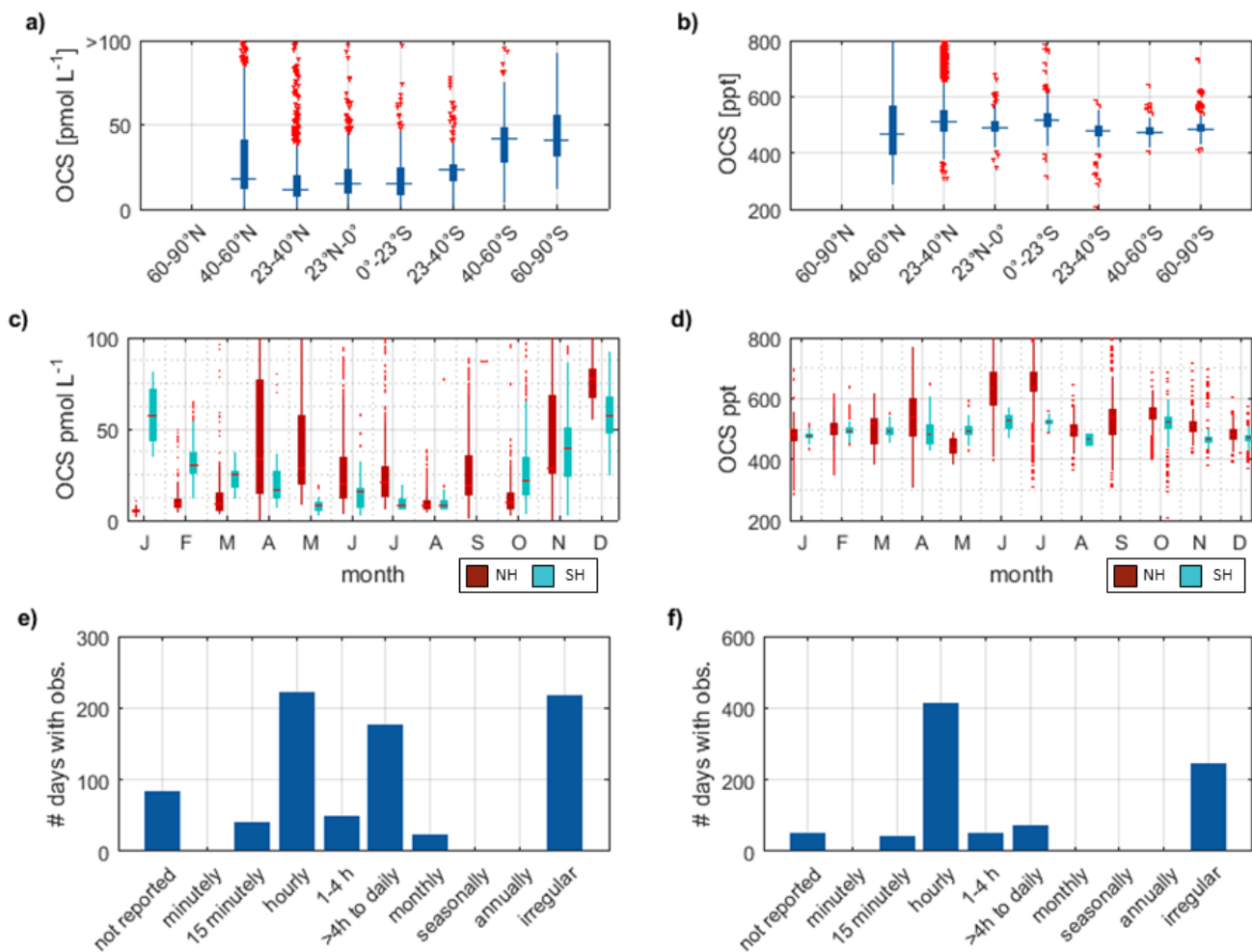
Figure 3: Overview of the OCS datasets: Boxplots of concentrations per latitudinal bin for a) water and b) marine boundary layer measurements. Blue boxes show range of 25 and 75 percentile, horizontal bar indicates the median, and red crosses show outliers. The seasonal variation averaged over all years for c) water and d) marine boundary layer (note that in panel c and d, red indicates Northern hemisphere data, whereas light blue indicates Southern hemisphere data. Note that measurements >150 pmol L^{-1} were excluded from these statistics (i.e. coastal samples). Numbers of days with observations for temporal resolution from minutely to annually for e) water and f) marine boundary layer measurements. (Note that for the boxplots in a) and b), only completely georeferenced data were included). NH=Northern hemisphere, SH=Southern hemisphere.
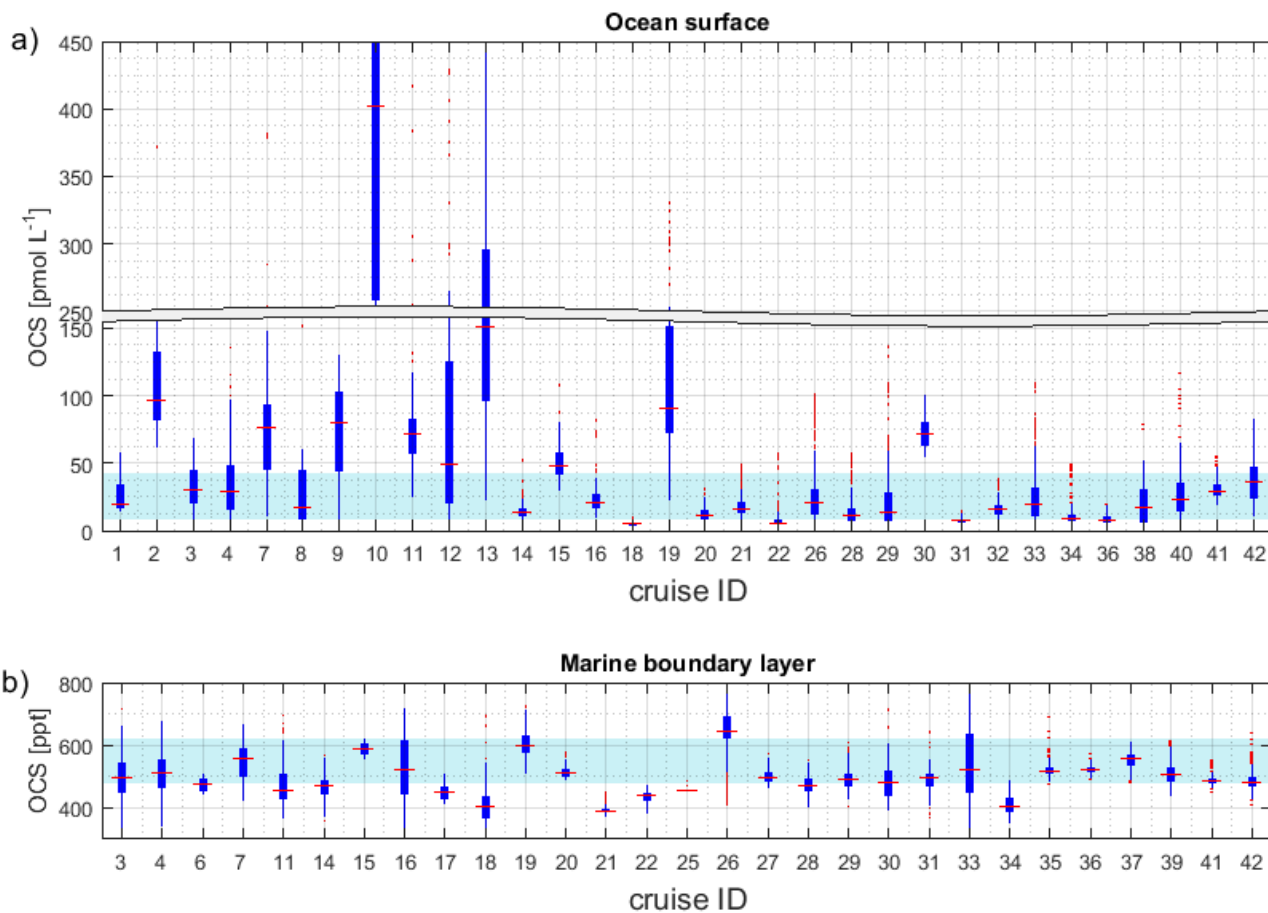
Figure 4: Boxplots of measured OCS concentrations in a) seawater and b) marine boundary layer. Marked in red is the median of each individual dataset, the edges of the box represent the 25th and 75th percentile, and outliers are indicated by red dots. The patch in the background indicates the 20th and 80th percentile of the whole dataset. Note the break in the y-axis in a).
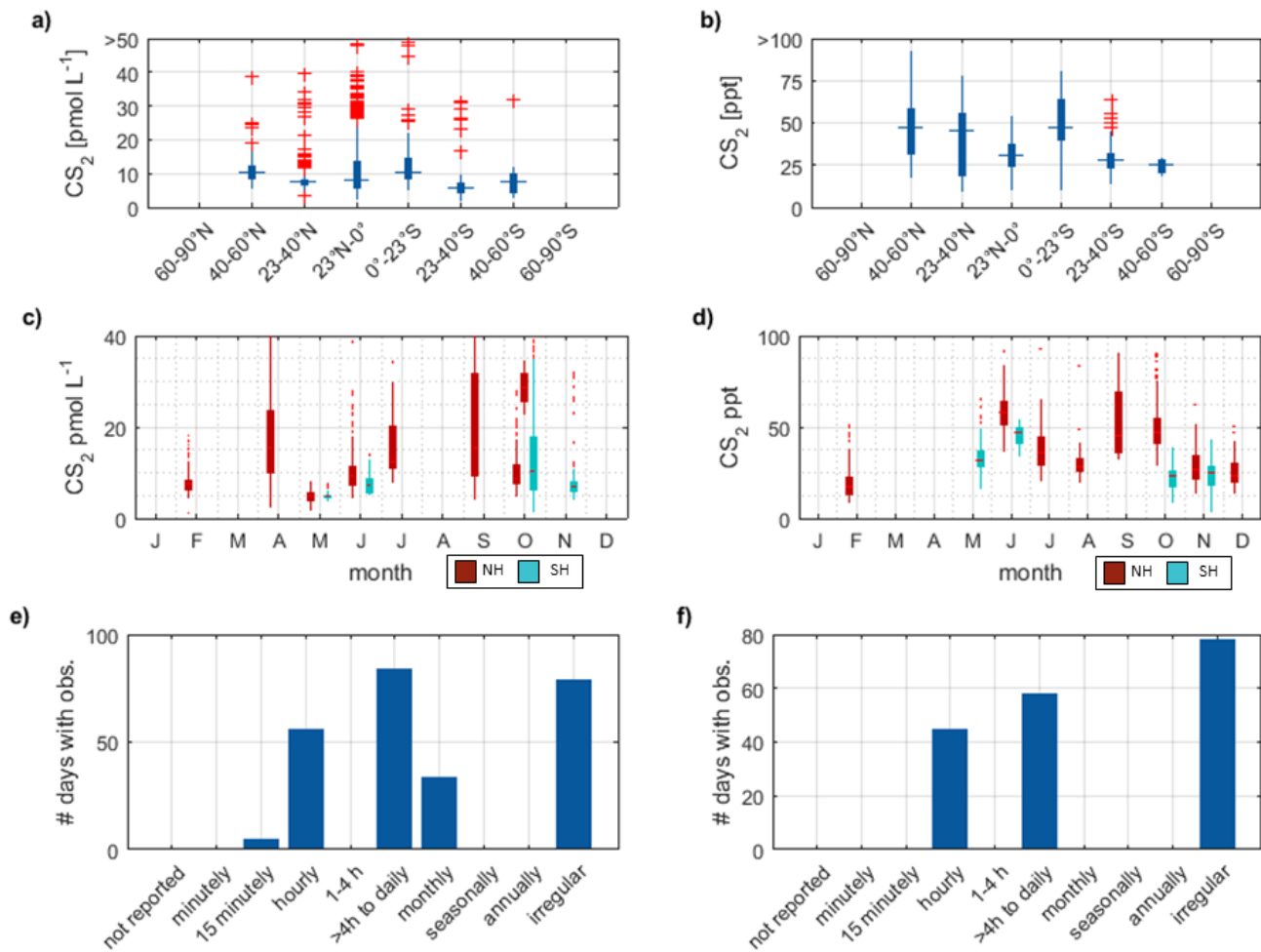
Figure 5: Same as Figure 2, but for CS₂.
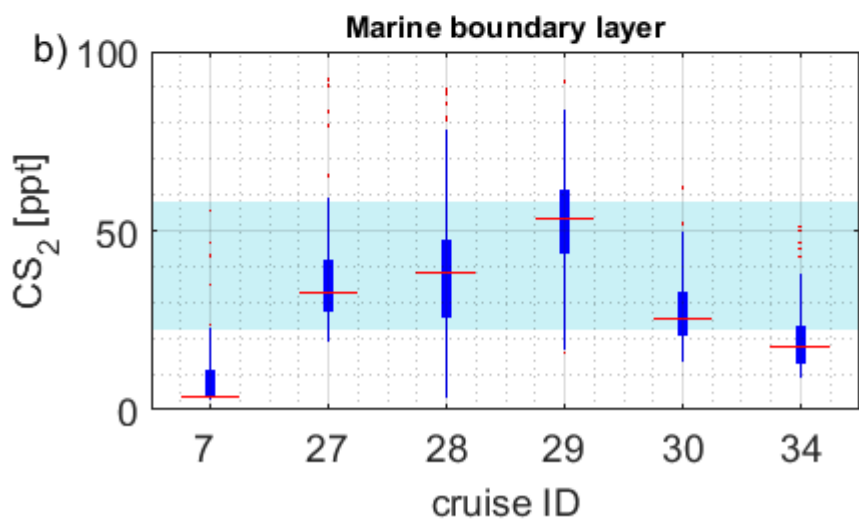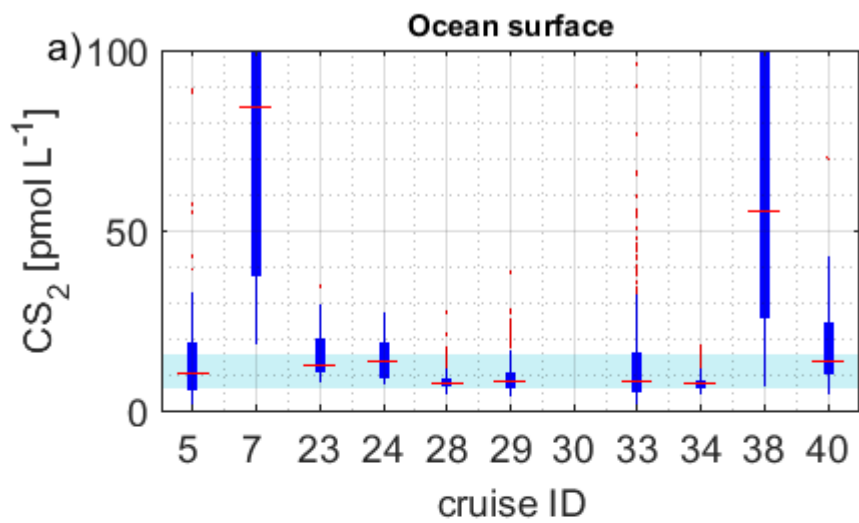
Figure 6 Same as Figure 4 but for CS₂.