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A simple method for air/sea gas exchange measurement in mesocosms and its application in carbon budgeting

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Abstract

Mesocosms as large experimental vessels principally provide the opportunity of performing elemental budget calculations e.g. to derive net biological turnover rates. However, the system is in most cases not closed at the water surface and gases can exchange with the atmosphere. Previous attempts to budget carbon pools in mesocosms relied on educated guesses concerning the exchange of CO_2 with the atmosphere. Nevertheless, net primary production rates derived from these budget calculations were, despite large uncertainties in air/sea gas exchange, often more reasonable than cumulative extrapolations of bioassays. While bioassays have limitations representing the full spectrum of trophic levels and abiotic conditions inside the mesocosms, calculating dissolved inorganic carbon uptake inside the mesocosms has the potential to deliver net community production rates representative of the enclosed system. Here, we present a simple method for precise determination of air/sea gas exchange velocities in mesocosms using N_2O as a deliberate tracer. Beside the application for carbon budgeting, exchange velocities can be used to calculate exchange rates of any gas of known concentration, e.g. to calculate aquatic production rates of climate relevant trace gases. Using an arctic (Kiel Off Shore Mesocosms for future Ocean Simulation) mesocosm experiment as an exemplary dataset, it is shown that application of the presented method largely improves accuracy of carbon budget estimates. Methodology of manipulation, measurement, data processing and conversion to CO_2 fluxes are explained. A theoretical discussion of prerequisites for precise gas exchange measurements provides a guideline for the applicability of the method under various experimental conditions.

1 Introduction

Pelagic mesocosms represent large volume (mostly between one and 10 m^3) experimental units used to gather experimental data on natural plankton communities (Petersen et al., 2003). Most mesocosm studies currently focus on investigating ecological interactions applying standard oceanographic methods on subsamples of the enclosed water. In principal, such experiments also provide the opportunity to understand biogeochemical element fluxes such as air/sea gas exchange and export. For this purpose, in situ measurements using the whole enclosure as experimental vessel have to be elaborated, in order to avoid problems occurring when extrapolating from bottle incubations to the mesocosm. But mesocosms are generally open towards the atmosphere allowing for air/sea gas exchange, making it difficult to calculate production or consumption of volatile compounds inside an experimental unit.

Climate relevant trace gases and other volatile carbon compounds produced in marine environments are increasingly investigated for their potential climate feedbacks and have been measured in previous mesocosm experiments (Sinha et al., 2007; Archer et al., 2012; Hopkins et al., 2012). Precise knowledge of air/sea gas exchange rates is needed, in order to compare measured aquatic concentrations of gases between various experiments or even with open ocean conditions, and to calculate turnover rates.

Not only in the context of global change, CO_2 entering the surface ocean, being fixed via photosynthesis, feeding the food chain and sinking into the ocean interior is of special interest to biogeochemical experimentalists. Calculating carbon fluxes from water column pools of inorganic and organic carbon quantitatively related to air/sea fluxes and export rates could largely improve the understanding of the system (Czerny et al., 2012a). For a direct integrated estimates of cumulative net community production, changes in CT have to be corrected for CO_2 air/sea gas exchange and eventually for calcification and evaporation. In previous mesocosm experiments in a Norwegian Fjord (Delille et al., 2005) and indoors (Wohlers et al., 2009; Taucher et al., 2012), net community carbon production (NCP), calculated on the basis of measured changes in total dissolved inorganic carbon (CT) were presented.

Delille et al. (2005) used a parameterisation for wind dependent boundary layer thickness achieved from experimental data compiled by Smith (1985) to calculate air/sea gas exchange. Wind speed, the crucial input parameter, was set zero, because the mesocosms were closed to the atmosphere and moored in a sheltered surrounding. Whereas most parameterisations result in zero gas exchange at zero wind speed (Wanninkhof, 1992), laboratory derived data by Smith et al. (1985) can be used to calculate air/sea gas exchange in calm environments. Under calm conditions, gas exchange is governed by other energy inputs than wind, e.g. thermal convection due to evaporation and temperature changes (Liss, 1973). Here, the general assumption was made that calm conditions in the mesocosm are comparable to the conditions in the experimental tanks used by Smith et al. (1985) to determine the boundary layer parameterizations. However, surface turbulence in many mesocosm experiments is unlikely to be very low. Active mixing systems, wave movement of the surrounding water, thermal mixing or the deployment of sampling gear might create turbulence within the enclosures, comparable to quite windy conditions. Taucher et al. (2012) for example, found wind speeds of more than $6\,\mathrm{m\,s^{-1}}$ to be necessary for balancing the carbon budget in a Kiel indoor mesocosm experiment, applying the Smith et al. (1985) calculation. While parameterisations for wind speed dependent gas exchange over the ocean are obviously not suitable for calculating mesocosm air/sea gas exchange, direct measurement of exchange velocities in an enclosed water volume can be easily done.

Here, we present a simple method for direct measurements of air/sea gas exchange rates in mesocosm experiments using N_2O as a tracer. The conversion of measured exchange rates to those of CO_2 and other gases is explained. We are providing a detailed description of the method and calculations including a discussion of prerequisites to achieve high quality data.

The measurement protocol and results are explained using a KOSMOS (Kiel Off Shore Mesocosm for future Ocean Simulation) (Fig. 1a) experiment on ocean acidification in the Arctic as a model. Applicability of the method in the Kiel indoor mesocosm facility is further explained and discussed.

2 Methods

2.1 N_2O addition

One litre of saturated N_2O solution was prepared via bubbling of seawater for two days in a narrow measurement cylinder covert with Parafilm®. Additions of the solution to the mesocosm were calculated using solubility constants by Weiss and Price (1980) with respect to salinities (S) and temperatures (T).

The targeted concentrations of N_2O should be adapted to the setup in order to achieve mesocosm to air fluxes, which can be measured at good precision over reasonable time scales. Here, seawater tracer concentrations were chosen in accordance to the highest certificated reference material for N_2O analyses available in our lab ($\sim 55\,\mathrm{nmol\,kg^{-1}}$).

Assuming a background concentration of $13\,\mathrm{nmol\,kg^{-1}}$, $40\,\mathrm{nmol\,kg^{-1}}$ of medical grade N_2O was added. Based on experience, a surplus of approximately 20 % was added to the mesocosms to account for losses unavoidable during handling of the solution.

Addition of the solution to the mesocosms (about $1–2\,\mathrm{ml\,m^{-3}}$) can be calculated according to the formulation:

$$V_{\mathrm{ad}} = \frac{V_{\mathrm{w}} \cdot \mathrm{ad}}{K_{\mathrm{TS}} \cdot 1000} \tag{1}$$

where V_{ad} is the volume of N_2O stock solution added (ml), V_{w} the volume of the mesocosm (l), (ad) the desired addition ($\mathrm{mol\,l^{-1}}$), and K_{TS} is the solubility constant by Weiss and Price (1980) for S and T of the N_2O stock solution ($\mathrm{mol\,l^{-1}\,atm^{-1}}$) prepared at one atmosphere.

A syringe with a large inlet diameter was used to transfer the stock solution carefully. Filling of the syringe was done slowly as vacuum increases undesired outgassing of N_2O. The stock solution was first diluted with filtered seawater in 25 l carboys, which were filled almost to the brim. The content of the carboys was homogeneously distributed to the mesocosms by using the pumped injection device "Spider" (Riebesell et al., 2012).

2.2 Sampling

Three of the nine mesocosms were sampled every second day using integrating water samplers (IWS, Hydrobios). Triplicate samples, representative for the 15 m deep water column, were drawn directly from the sampler. The water was filled bubble free into 50 ml headspace vials via a hose reaching to the bottom of the vial. The vial volume was allowed to overflow about four times before closing. Vials were closed with butyl rubber plugs (N20 Machery and Nagel), crimp sealed and stored at room temperature after addition of 50 µl of saturated mercury chloride solution.

2.3 Measurement procedures

Measurement of aquatic N_2O concentrations was performed via gas chromatography with electron capture detection (Hewlett Packard 5890 II), using a headspace static equilibration procedure as described by Walter et al. (2006). The GC was equipped with a 6'/1/8" stainless steel column packed with a 5 Å molecular sieve (W. R. Grace and CO) and operated at a constant oven temperature of 190 °C. A 95/5 argon-methane mixture (5.0, Air Liquide) was used as carrier gas. 10 ml of helium (5.0, Air Liquide) headspace was added and manually injected after equilibration was achieved by manual shaking and storage for at least 10 h at equilibration temperature of 21 °C. Certified gas mixtures (Deuste Steininger GmbH) with mixing ratios of 87.2, 318 and 1002 ppb as well as 1 : 1 dilutions with helium were used to construct calibration curves with a minimum of three data points close to sample concentrations. Headspace to water phase ratios in the vials was determined gravimetrically.

Dissolved inorganic carbon was determined via colorimetric titration using a SOMMA system and total alkalinity (TAlk) via potentiometric titration (Dickson, 1981). CO_2 concentrations, partial pressures and pH (total scale) were calculated from DIC and TAlk measurements with the program CO2SYS by Lewis and Wallace (1995). For more details on carbonate chemistry see Bellerby et al. (2012).

Determination of salinity and temperature in the mesocosms was performed with a data logger-equipped hand held multisensory CTD 60M (Sea and Sun Technology). Volume of the mesocosms was determined with the same instrument using sodium chloride additions of ~ 0.2 g kg^{-1} as a tracer (Czerny et al., 2012b).

Wind velocity and direction measured at 10 m height onshore about one mile from the mooring site were provided by the staff of the AWI-PEV Station in Ny Ålesund.

2.4 Setup of the Svalbard 2010 ocean acidification experiment

Nine 15 m deep KOSMOS mesocosms each with a diameter of 2 m were moored end of May 2010 in the Kongsfjorden, Svalbard. Seven different CO_2 treatment concentrations were achieved through addition of CO_2 saturated seawater. While the ambient (~ 180 µatm pCO_2) control treatment was replicated twice, the seven enriched mesocosms followed a gradient up to ~ 1420 µatm pCO_2. Development of the enclosed natural plankton community was followed for 30 days after CO_2 manipulation, including addition of inorganic nutrients on day 13. For more details see Riebesell et al. (2012) and Schulz et al. (2012).

3 Results and discussion

Concentrations of N_2O added on day four decreased in the enriched mesocosms from initially measured ~ 50 nmol kg^{-1} on day 6 to ~ 30 nmol kg^{-1} on day 28 (Fig. 1b).

Concentrations measured in the fjord close to the mesocosms were slightly oversaturated compared to atmospheric equilibrium values, calculated for in situ seawater T, S and atmospheric mixing ratios measured close by on Zeppelin Mountain. Despite variable wind conditions, the concentration decrease inside the mesocosms could be fitted ($R^2 = 0.96$) using the relationship:

$$C_{N_2O} = 60\,556 \cdot e^{-0.0241 \cdot d} \tag{2}$$

3.1 Calculation of CO_2 fluxes from changes in N_2O concentrations

Daily N_2O fluxes were calculated from the fitted N_2O concentration decrease over time and converted to volumetric units. Changes in the N_2O inventory, derived using the determined volume of the mesocosms (method described in Czerny et al., 2012b) were used to calculate fluxes in µmol cm^{-2} h^{-1} (F_{N_2O}) across the water surface according to:

$$F_{N_2O} = \frac{I_{w_1} - I_{w_2}}{A \cdot \Delta t} \tag{3}$$

where I_{w_1} is the fitted bulk water N_2O inventory in µmol per mesocosm on t_1 and I_{w_2} on t_2 with Δt as the time interval between t_1 and t_2 in h, while A is the nominal surface area of the mesocosm in cm^2. A N_2O transfer velocity (k_{N_2O}) in cm h^{-1} is than calculated by dividing F_{N_2O} by the concentration gradient according to Eq. (4):

$$k_{N_2O} = \frac{F_{N_2O}}{(C_{N_2Ow} - C_{N_2Oaw})} \tag{4}$$

where C_{N_2Ow} is the fitted bulk water N_2O concentration (µmol cm^{-3}) at the point in time and C_{N_2Oaw} the calculated (Weiss and Price, 1980) equilibrium concentration of N_2O with the atmosphere at prevailing bulk water T and S. k_{N_2O} can be translated into a transfer velocity for any other gas using its Schmidt numbers to correct for gas specific properties as shown for the transfer coefficient of CO_2 (k_{CO_2}) in Eq. (5):

$$k_{CO_2} = \frac{k_{N_2O}}{\left(\frac{Sc_{CO_2}}{Sc_{N_2O}}\right)^{0.5}} \quad (5)$$

The Schmidt number for N_2O (Sc_{N_2O}) published by Rhee (2000), and the Schmidt number for CO_2 (Sc_{CO_2}) derived from diffusion coefficients published by Jähne et al. (1987) were used. Fluxes for CO_2 (F_{CO_2}) can then be calculated by multiplication of k_{CO_2} with the diffusion gradient between bulk water CO_2 concentrations and calculated equilibrium concentrations with the atmosphere as:

$$F_{CO_2} = k_{CO_2} \cdot (C_{CO_2w} - C_{CO_2aw}) \quad (6)$$

3.2 Chemical enhancement of CO_2 air/sea gas exchange

Another correction has to be applied to derive accurate CO_2 fluxes in calm environments like the KOSMOS mesocosms. As CO_2, reacts with water, unlike N_2O, CO_2 gas exchange might be chemically enhanced due to buffering of diffusive concentration change by equilibration reactions within the boundary layer. Other than inert gases, exchanged CO_2 diffuses not necessarily through the boundary layer, but can be also formed from bicarbonate close to the interface. This applies only at low wind speeds due to slow CO_2 hydration kinetics, and not when mixing is considerably faster. Thus, chemical enhancement is thought to be insignificant under turbulent conditions relevant for open ocean CO_2 exchange (e.g. when $k > 5\,\text{cm}\,\text{h}^{-1}$), but applies to the conditions found inside the mesocosms ($k \sim 1.8$–$2.5\,\text{cm}\,\text{h}^{-1}$) (Wanninkhof et al., 1996). Moreover, the state of the carbonate system determines the extent of chemical enhancement, being negligible at $\text{pH} < 6$ and substantial at $\text{pH} > 8$. In the Svalbard ocean acidification experiment, the treatment pH_{tot} (total scale) ranged from 7.5 to 8.3 (Bellerby et al., 2012), therefore chemical enhancement created a pH effect on carbon flows that must be considered. To correct for this, theoretical parameterisations by Hoover and Berkshire (1969) were chosen, as currently no empirical parameterisations exist sufficiently describing the process in natural seawater (Wanninkhof et al., 1996). The enhancement factor α, the ratio between chemical enhanced flux and not enhanced flux can be calculated using Eq. (7):

$$\alpha = \frac{\tau}{\left[(\tau - 1) + \tanh Qz/Qz\right]} \tag{7}$$

here, dimensionless $\tau = 1 + \left[H^+\right]^2 \left(K_1^* K_2^* + K_1^* \left[H^+\right]\right)^{-1}$, with K_1^* and K_2^* being the first and second stoichiometric equilibrium constants for carbonic acid and $\left[H^+\right]$ the proton concentration. $Q = \left(r\tau D^{-1}\right)^{0.5}$ in cm^{-1}, where $r = r_1 + r_2 K_\text{w}^* \left[H^+\right]^{-1}$ (s^{-1}), with r_1 being the CO_2 hydration rate constant for reaction two (s^{-1}) and r_2 is the rate constant for reaction three ($\text{l}\,\text{mol}^{-1}\,\text{s}^{-1}$) from Johnson (1982) and K_w^* is the equilibrium constant for water. D is the diffusion coefficient for CO_2 by Jähne et al. (1987). The boundary layer thickness z (cm) can be calculated from determined transfer velocity ($z = D\, k_{CO_2}^{-1}$). All constants used here can be found in Zeebe and Wolf-Gladrow (2001). Using the Hoover and Berkshire (1969) model, input conditions similar to our experimental conditions in Svalbard ($T = 5\,^\circ\text{C}$, $S = 35$, $z = 0.002\,\text{cm}$, $\text{pH}_\text{tot} = 8.2$) result in enhancement of about 8 % ($\alpha = 1.082$). For the same conditions, but at a temperature of 25 °C, CO_2 gas exchange would be enhanced by about 48 % ($\alpha = 1.479$).

Chemical enhancement factors using more complex models published by Smith (1985), Emerson (1975), Quinn and Otto (1971), and Keller (1994) give very similar results to the Hoover and Berkshire (1969) model (Wanninkhof et al., 1996). Experimental data from tank experiments reproduce calculated chemical enhancement relatively well, i.e. Hoover and Berkshire, (1969), Wanninkhof et al., (1996), Degreif (2006), Liss (1973). The simple fit derived from enhancement experiments in natural Baltic seawater published by Kuss and Schneider (2004) is not recommended for use, as influences of T, S and z are not considered.

The relevance of chemical enhancement for ocean CO_2 exchange is controversial as the calculation of k from wind speed over the ocean itself still bears considerable uncertainty. As k in our experiments is measured directly, comparability to experimental results is quite straight forward.

Due to low temperatures during the Svalbard experiment, chemical enhancement of ~3 to 7 % is very low (Fig. 6). The influence of about 3 degree warming during the experiment in June 2010 is overall larger than the calculated difference arising from pH treatments (Fig. 3). Strong pH-dependent chemical enhancement could produce artificial treatment effects in the carbon budget estimates especially in ocean acidification studies. Biological carbon uptake estimates by Silyakova et al. (2012) and Czerny et al. (2012a) at arctic temperatures are relatively unaffected by enhancement of this magnitude and possible uncertainties therein.

Evidence for a strong increase in chemical enhancement due to enzymatic catalysis by free carbonic anhydrases as suggested by Berger and Libby (1969) was not found in later experiments (Goldman and Dennett, 1983; Williams, 1983), but it might be interesting to reconsider this question in future mesocosm experiments.

The lack of empirical data coverage on chemical enhancement parameterisations in seawater poses the major quantitative uncertainty for NCP estimates based on CO_2 air/sea gas exchange using the presented method. Especially in setups were temperatures are high, the proportion of CO_2 exchange relying on theoretical considerations is high compared to the directly measured flux.

3.3 Potential errors and uncertainties

Analytical errors in N_2O fluxes were small, calculated on the basis of standard deviation of the measured values around the fit ($\pm 1.54\,\mathrm{nmol\,kg^{-1}}$). Resulting uncertainty in the determination of daily CO_2 fluxes are shown as error bars in Fig. 2. Here, k for maximum and minimum N_2O results were used to calculate CO_2 fluxes.

Underlying variability in CO_2 fluxes shown in Fig. 2 is caused by variability in measured aquatic CO_2 concentrations, responsible for the CO_2 diffusion gradient. The uncertainty in fluxes caused by errors in carbonate system determination seem to be of similar magnitude or larger than the error introduced from N_2O analytics.

The natural source of oceanic background N_2O concentrations is biological production. N_2O is produced predominantly as a side product of nitrification, when ammonia is incompletely oxidised in the course of deep remineralisation at low oxygen concentrations. Yet, most parts of the ocean are near equilibrium with the atmosphere (mean global saturation 103 %) (see Bange et al. (1996) and references herein), whereas N_2O oversaturation is predominantly found in tropical regions rather than in cold and temperate waters (Walter et al., 2006).

Detectable nitrification in the euphotic zone was hypothesised to be also a source of N_2O (Dore and Karl, 1996; Santoro et al., 2010), but this was not yet directly observed. Physiological results (Goreau et al., 1980; Loescher et al., 2012) suggest possible N_2O production by nitrification in fully oxygenated waters to be very low. However, even relatively high surface layer nitrification rates, as found in upwelling regions (Rees et al., 2011), are orders of magnitudes to low to significantly bias the large fluxes caused by deliberate N_2O addition. Remineralisation of detritus at the bottom of the mesocosm could possibly be a source of N_2O. Conditions allowing for extensive remineralisation of accumulated organics inside pelagic mesocosms should thus be avoided. It is further strongly recommended to measure background natural N_2O concentrations preferably inside non enriched experimental units, because N_2O is not considered as an inert gas.

Due to convection caused by slight temperature changes in the surrounding water (Fig. 4) and an evaporation induced salinity increase (Schulz, 2012), the mesocosms in the Svalbard KOSMOS study could be considered to be homogeneous on timescales relevant for air/sea gas exchange. For referring from N_2O fluxes to those of inert gases, it might be irrelevant whether exchange is limited by mixing processes on the air sea interface or within the water column. Yet, if a permanent stratification is formed inside the mesocosm, the decrease of N_2O bulk water concentration can not be used to calculate mesocosm-atmosphere CO_2 exchange. Processes modulating the concentrations of biologically active compounds such as CO_2 are usually variable along the light gradient. Therefore, due to shallow primary production, considerable differences in the surface gradient of CO_2 might emerge compared to N_2O surface gradients that are governed by diapycnal mixing. For stratified mesocosms, gas exchange calculations require the integration of information about vertical distribution of tracer and gases of interest. Therefore, N_2O inventories have to be determined by integrated water samples independently from surface gradients determined from discrete surface water samples.

For the experiments in the KOSMOS mesocosms, gas permeability can be neglected as the bag material used is 0.5 to 1 mm thick. Estimates based on (Desmopan® 385, Bayer) the raw material of our bag foil (Walopur®, Epurex Films) revealed that the fraction of lateral gas exchange trough the bag were in the order of 1–2 % of the total flux. Differences between N_2O and CO_2 in the material specific permeability of the thermoplastic polyurethane used to manufacture the bags could have the potential to cause systematic errors. Such differences seemed at first unlikely because of the general similarity of N_2O and CO_2 in diffusivity and solubility, but permeability specifications for Desmopan 385 suggest a considerably higher permeability for N_2O (Bayer MaterialScience, TPU TechCentre). If thin foil is used for mesocosms, a material with good gas barrier properties should be chosen and exact permeabilities should be known for the gases of interest.

When k_{N_2O} is translated into transfer velocities of poorly soluble gases, dissolution and adhesion of some organic compounds in and on the plastic material could cause a lateral sink of these substances additionally to the permeability issue.

3.4 Processes driving gas exchange in mesocosms

The concentration of N_2O (C_{N_2O}) decreased quite steadily over the whole experimental period (Fig. 1b). This indicates that N_2O fluxes were controlled by the diffusion gradient to the atmosphere. Variable external forcing by wind or waves as commonly observed in natural environments was of minor importance. Wind measurements at Bellevaja station at 10 m above sea level reported velocities of up to 5 m s^{-1} during the experiment (Fig. 5). The water surface of the mesocosms, however, is sheltered from direct wind sheer by the two meter high plastic walls of the bag (Fig. 1a; Riebesell et al., 2012).

Waves that were able to propagate through the mesocosms were only observed on the mooring site on three days when stronger winds were blowing along the fjord from southeast, the most exposed wind direction. Enhanced gas exchange during three days with waves of ~60 cm could not be resolved by our measurements. However, CO_2 gas exchange inside the mesocosms was here measured to be consistently about three times higher than calculated flux at zero wind (Fig. 6, stagnant film thickness calculated according to Smith, 1985, chemical enhancement according to Hoover and Berkshire, 1969) as performed by Delille et al. (2005).

Applying a quadratic wind depended function (Wanninkhof, 1992) at constant wind speed of 3.15 m s^{-1}, resulting fluxes are very close to our empirical estimate over the whole period. Measured wind speeds during the experiment were generally lower than this (mean 2.1 m s^{-1}), and accordingly calculated mean air/sea gas exchange was also lower outside than inside the mesocosms. This suggests different processes to be driving gas exchange in mesocosms compared to open waters. Rinsing of the plastic walls when waves are propagating through the setup presumably leads to enhanced surface renewal compared to open water. Slight temperature changes in the surrounding water mass were immediately heating or cooling the bags (Fig. 4), this probably caused a considerable thermal convection that kept the experimental units relatively homogenous throughout the experiment. Last but not least the extensive daily sampling with water samplers and probes contributed to gas exchange by active perturbation of the mesocosm surface.

3.5 Mesocosm proportions

Exchange velocities (k) in other mesocosm setups deployed in more sheltered surroundings, standing on land or inside climate controlled rooms might be lower or higher, depending on methodology used for sampling, temperature control, active mixing and gas specific permeability of the mesocosm material. Even more important than these influences on k, is the ratio between the mesocosm volume and its surface area (A/V), when exchange rates are normalised to units of water (kg^{-1} or l^{-1}). In an exemplary 15m deep KOSMOS mesocosm (Fig. 1a), holding ~45 m^3 of water, CO_2 gas exchange over 3.14 m^2 ($A/V = 0.07$) surface area is causing relatively moderate changes in aquatic concentrations despite large diffusion gradients (Fig. 2). Taking the example of the Kiel indoor mesocosm (Fig. 7a) of about 1.4 m^3 at 2 m^2 surface ($A/V = 1.4$), concentration change in response to the same gas exchange flux is orders of magnitude faster. Additionally, air/sea gas exchange velocities are accelerated by continuous active mixing, necessary to keep plankton organisms in suspension (Fig. 7a). While after 20 days ~50 % of the N_2O added was still present during the Svalbard study (Fig. 1b), the same tracer concentration was virtually gone after 5 days in the shallow indoor mesocosm (Fig. 7b). Here, inorganic carbon uptake by phytoplankton can be rapidly compensated by ingassing of CO_2 from the atmosphere. Ocean acidification experiments in setups with A/V similar to the Kiel indoor mesocosm would lose their treatment CO_2 within a few days. Therefore, treatment levels in such experiments might be maintained using continuous measurement and control technology. Resulting controlled treatment levels are beneficial when physiological questions are investigated. However, CO_2 drawdown does not occur, and therefore DIC concentration change cannot be used to calculate NCP. Another option is to artificially decrease the surface area by covering the mesocosm with a low permeability transparent film. A thin polyurethane foil mounted on a light frame and floating on the surface, efficiently minimised air/sea gas exchange (Fig. 7a). Samples were drawn through a tube build into this cover. If covers are used, reducing the surface area to a minimum, it has to be considered that the remaining open surface should be equally large. Detailed data on this issue are missing, but as it can be imagined that this approach is very sensible to the size of the remaining interface, air/sea gas exchange should be measured in all experimental units.

4 Conclusion and outlook

Direct measurement of N_2O air/sea gas exchange can be used to estimate accurate CO_2 fluxes in various mesocosm setups, whereas common parameterisations for air/sea gas exchange are difficult to adapt to mesocosm conditions and are therefore prone to systematic errors. The commonly used parameterisations are also prone to large errors in open waters when applied on a local scale especially in productive coastal waters (Wanninkhof, 1992; Liss, 1973), although, they reproduce global CO_2 fluxes fairly well. Even problems usually present when estimating open ocean air/sea gas exchange using parameterisations are empirically solved by measuring transfer velocities (k) directly. The influence of sea surface microlayers of surface active organic molecules is discussed to be responsible for large discrepancies in gas exchange between productive coastal waters and open-ocean conditions (Frew, 1997; Kock et al., 2012). The effect of these surfactants, possibly produced in high amounts during phytoplankton blooms in mesocosms, is difficult to include in theoretical calculations, but inherently included in direct measurements. Future mesocosm experiments combining the close observation of biological, chemical and physical processes might offer the chance to bring more light into origin and composition of organic surface microlayers.

Of the four community production estimates published for the Svalbard 2010 experiment, NCP calculated from changes in dissolved inorganic carbon corrected for air/sea gas exchange (Czerny et al., 2012a; Silyakova et al., 2012) seems to be quantitatively most plausible. Although, overall quantity compares relatively well with results from oxygen and in situ ^{13}C-primary production estimates (Tanaka et al., 2012; de Kluijver, 2012), comparability to ^{14}C incubation data presented by Engel et al. (2012) is week. Much higher ^{14}C fixation rates can be plausibly explained by the shallow (~ 1 m) incubation depth, while oxygen incubations obviously experienced more intermediate light and temperature conditions at ~ 4 m depth. Therefore, bioassays are more useful to compare community production between the treatments rather than giving quantitative cumulative estimates for in situ carbon uptake (Tanaka et al., 2012). As incubations were performed only at one depth, it is impossible to integrate these data over time and depth in respect of variable light and temperature gradients. Summing up incubation results to achieve cumulative estimates would lead to further error propagation, whereas NCP calculated from in situ inorganic carbon measurements is per se cumulative and propagation of single measurement errors cannot occur.

Further development of the N_2O tracer concept is focussed on using it not only to determine air/sea gas exchange in stratified mesocosms, but also to estimate diapycnal mixing between surface layer and deep water inside mesocosms. For this purpose, N_2O gradients developing over time, will be correlated to high resolution profiles of oxygen pH and salinity, measured with CTD sensors. Especially in temperate turbid waters, surface layer production is mostly not restricted by mesocosm length but by light penetration. The photoautotrophic surface layer communicates to some extent with a more nutrient rich deep layer where heterotrophic processes dominate. Budgeting these more naturally structured mesocosms is not only an interesting challenge, but will also introduce new ecological aspects connected to upward and downward elemental fluxes into the biogeochemical interpretation of the mesocosm system.

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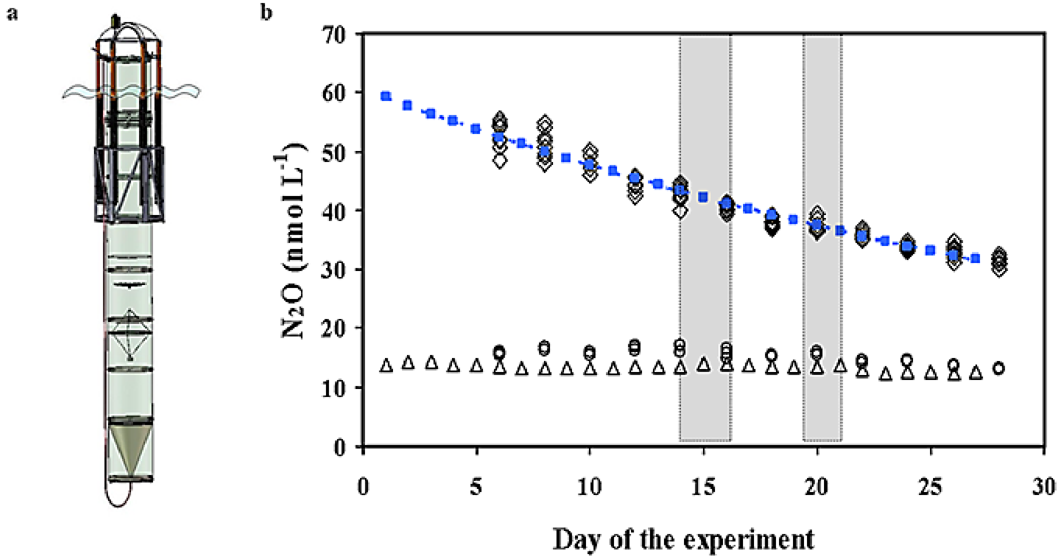

Fig. 1. (a) Drawing of a KOSMOS mesocosm in the configuration used for the Svalbard experiment. **(b)** N_2O concentrations during the experiment. Diamonds represent the measured concentration inside the 3 examined mesocosms; blue squares are fitted daily concentrations according to Eq. (2), circles are background N_2O concentrations measured in the surrounding fjord, triangles are calculated equilibrium concentrations from atmospheric measurements at in situ T and S. Shaded areas indicate periods when waves occurred at the mooring site.

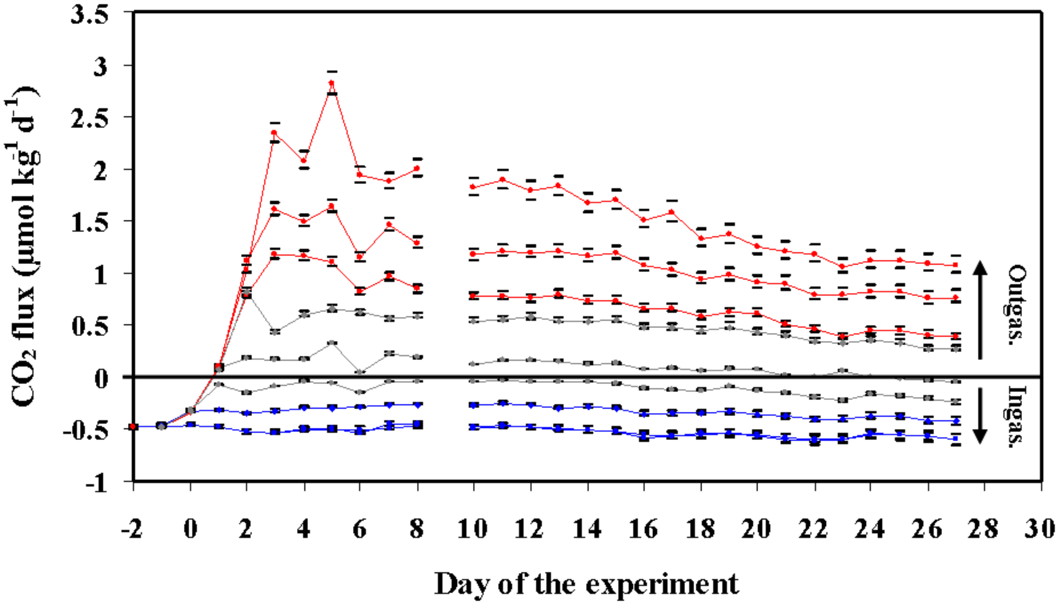

Fig. 2. Daily CO_2 fluxes for all CO_2 treatments over time. High CO_2 treatments are shown in red, medium in gray and low CO_2 are blue. Black error bars depict uncertainties derived from analytical uncertainties in N_2O analyses, calculated as the standard deviation of measured values around fitted values as shown in Fig. 1b.

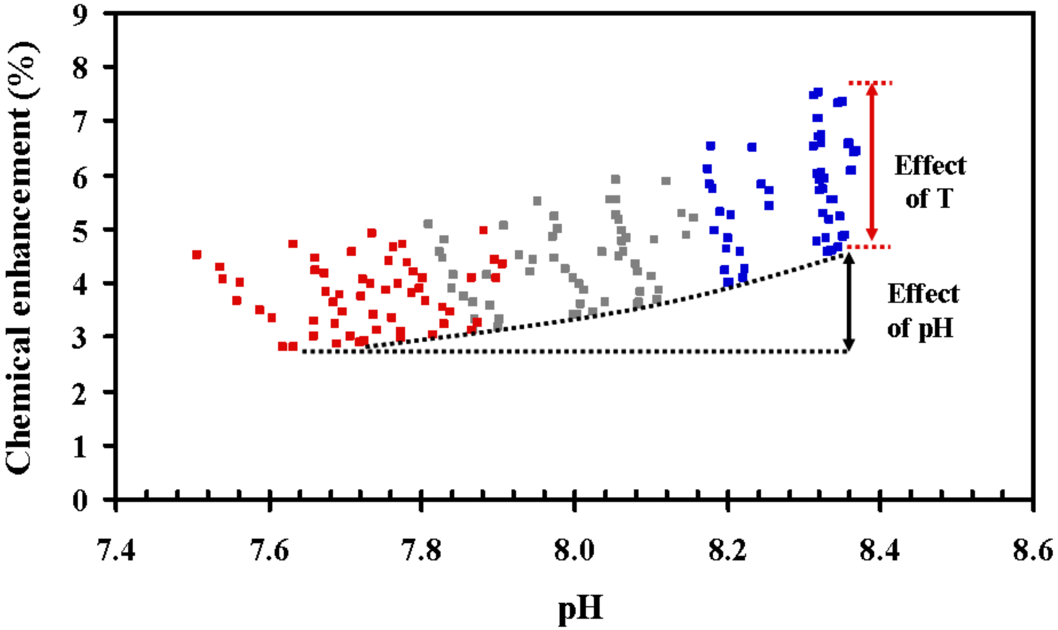

Fig. 3. Chemical enhancement of CO_2 compared to N_2O according to Hover and Berkshire (1969) calculated for measured k, S, T and pH_{tot} during the Svalbard experiment. High CO_2 treatments are red, medium are gray and low CO_2 are blue. The effect of pH_{tot} on chemical enhancement is indicated by the black arrow, while the effect of the ~ 3 °C temperature increase during the experiment is indicated by the red arrow.

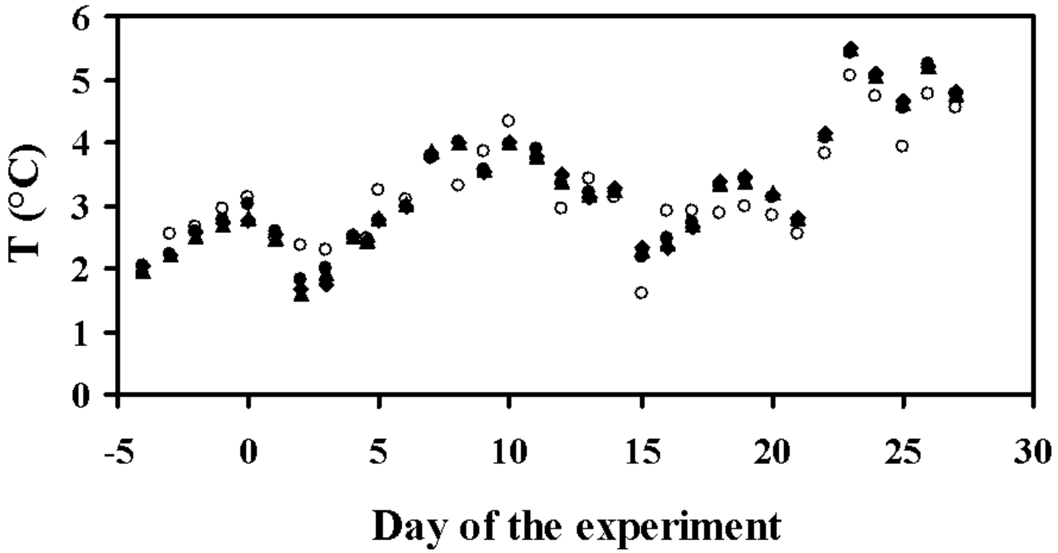

Fig. 4. Mean water temperatures between 0–12 m measured during the Svalbard experiment. The three examined mesocosms are shown as black symbols, while open circles represent measurements from the surrounding fjord.

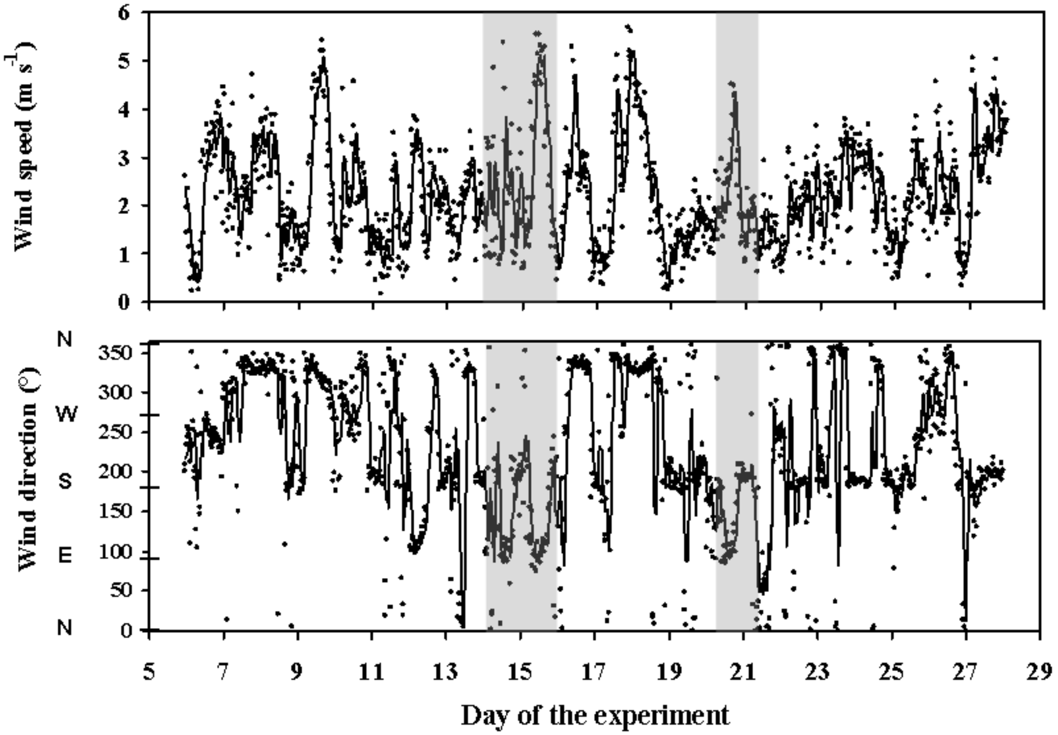

Fig. 5. Wind speed and direction during the course of the experiment, measured at 10 m height at Bayelva station, Ny Ålesund. Waves were observed at the mooring site during time intervals indicated by shaded areas, when relatively strong wind was blowing along the fjord from south east.

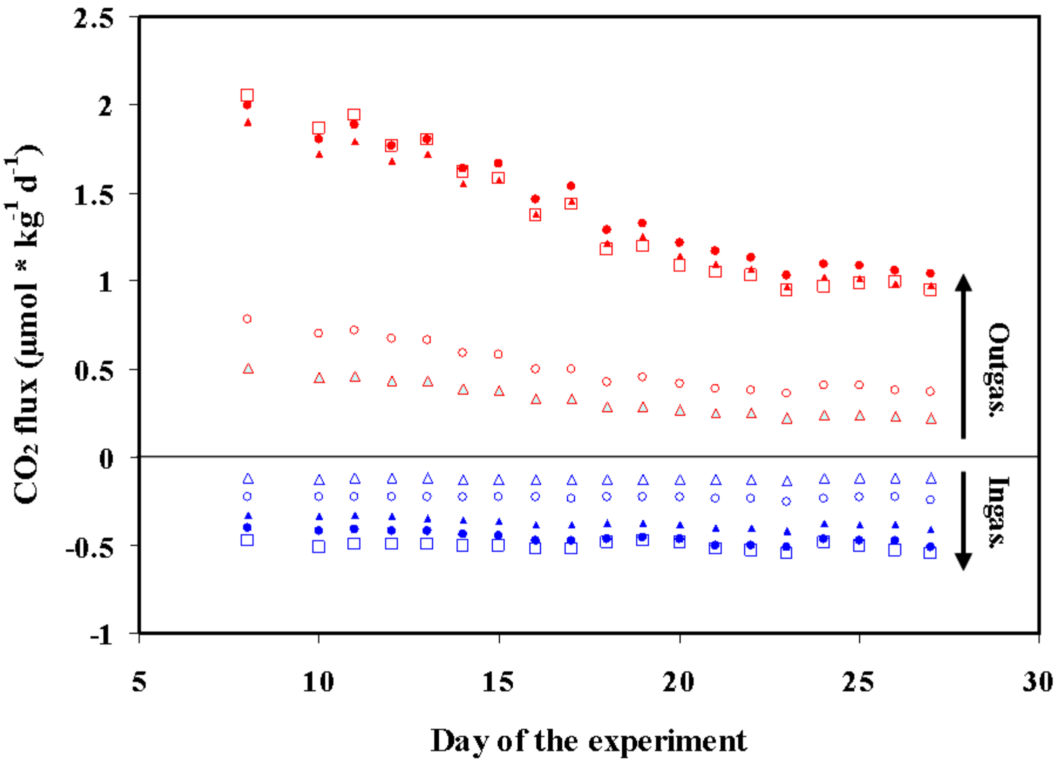

Fig. 6. Comparison of different approaches to estimate CO_2 air/sea gas exchange. Daily ingassing rates in the low CO_2 control treatment (average ∼ 180 µatm) are shown in blue, while outgassing from the highest CO_2 treatment (average ∼ 1085 µatm) is red. Filled symbols are estimates from the N_2O tracer approach, circles for chemical enhanced flux and triangles for non chemical enhanced flux. Open squares are an estimate using a quadratic wind dependent function according to Wanninkhof (1992) at a constant wind speed of 3.15 m s^{-1}, chosen to match the N_2O results. Open circles is a chemically enhanced zero wind speed output, according to Smith (1985), while open triangles are the same estimate without chemical enhancement.

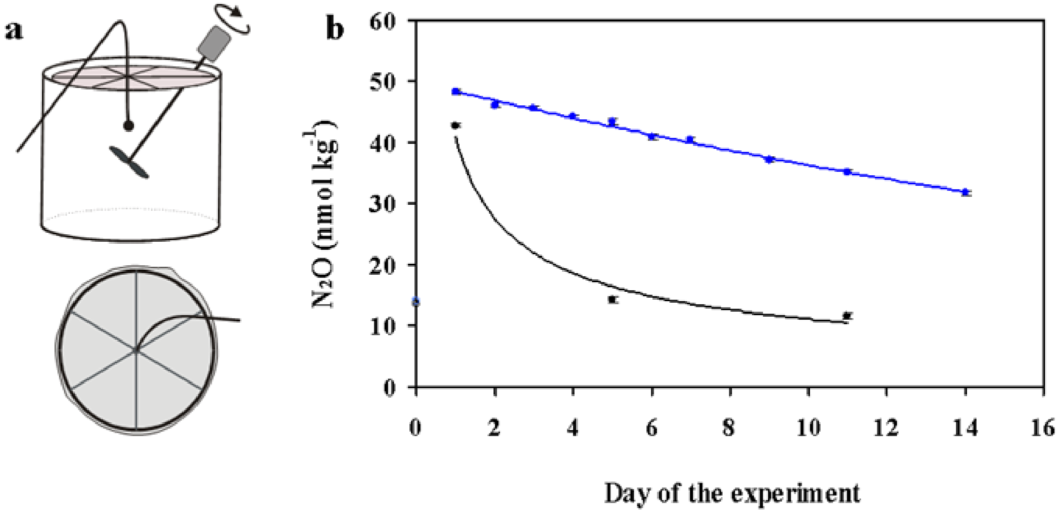

Fig. 7. (a) Schematic drawing of the Kiel indoor mesocosm. With stirrer, floating lid and sampling hose, below: vertical view on floating foil lid with enforcement frame. **(b)** Comparison of N_2O tracer outgassing in a Kiel indoor mesocosm, between a simple uncovered setup (black) and a setup using a floating foil lid reducing the water surface area available for air/sea gas exchange (blue).