



Technical Note: A simple method for air–sea gas exchange measurements in mesocosms and its application in carbon budgeting

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Abstract. Mesocosms as large experimental units provide the opportunity to perform elemental mass balance calculations, e.g. to derive net biological turnover rates. However, the system is in most cases not closed at the water surface and gases exchange with the atmosphere. Previous attempts to budget carbon pools in mesocosms relied on educated guesses concerning the exchange of CO₂ with the atmosphere. Here, we present a simple method for precise determination of air–sea gas exchange in mesocosms using N₂O as a deliberate tracer. Beside the application for carbon budgeting, transfer 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 KOSMOS (Kiel Off Shore Mesocosms for future Ocean Simulation) experiment as an exemplary dataset, it is shown that the presented method improves accuracy of carbon budget estimates substantially. Methodology of manipulation, measurement, data processing and conversion to CO₂ 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 fifty m³) experimental enclosures used to gather data on natural plankton communities (Petersen et al., 2003). Generally open towards the atmosphere, mesocosms, however allowing for air–sea gas exchange, make it difficult to calculate production or consumption of CO₂ and other volatile compounds inside an experimental unit. Climate rel-

evant 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). Observed concentrations in a mesocosm are a product of water-column reactions and losses or gains from the atmosphere. Precise knowledge of air–sea gas exchange rates can be used to calculate net production rates of these compounds in the water column, which can be compared between various experiments. Aquatic production rates in concert with data on biological community composition and physiological state would help to understand observed open-ocean distributions.

Not only in the context of global change, biological CO₂ fixation and consequent carbon export by sinking particles is of special interest to biogeochemical experimentalists. Most mesocosm studies currently focus on investigating ecological interactions applying standard oceanographic methods on subsamples of the enclosed water. In principal, mesocosm experiments also provide the opportunity to compare biogeochemical element fluxes such as air–sea gas exchange and export to water-column production. With production rates, as usually measured in side experiments (e.g. O₂ production or ¹⁴C incorporation), uncertainties arise from sample transfer into bottle incubations and from extrapolating back from incubation conditions to temperature and light gradients present in mesocosms. In situ primary production measurements using the whole enclosure as experimental vessel have to be elaborated, in order to produce estimates comparable to total mesocosm fluxes like sedimentation of organic matter. 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). To directly estimate cumulative net community production (NCP), changes in total dissolved inorganic carbon (CT) have to be corrected for CO₂ 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 production (NCP), calculated on the basis of measured changes in CT, were presented. To calculate air–sea gas exchange, Delille et al. (2005) used a parameterisation for wind dependent boundary layer thickness achieved from experimental data compiled by Smith (1985). Wind speed, the crucial input parameter, was set to 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 wind dependent parameterisations by Smith et al. (1985) resulted in positive exchange at zero wind speed. Under calm conditions, gas exchange is low, but not zero; it is governed by other energy inputs than wind, e.g. thermal convection due to evaporation and temperature changes (Liss, 1973; Wanninkhof et al., 2009). Although direct wind forcing might be negligible in most mesocosms, the general assumption that overall energy input is comparable to the conditions in the experimental tanks used by Smith et al. (1985), however, is not justifiable. 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 m s⁻¹ to be necessary for balancing the carbon budget in a Kiel indoor mesocosm experiment, applying the Smith et al. (1985) calculation. Parameterisations for wind speed dependent gas exchange over the ocean are obviously not suitable for calculating mesocosm air–sea gas exchange. Other than open-ocean gas exchange measurements, direct measurement of exchange velocities in an enclosed water volume can be relatively easily done.

Here, we present a simple method for direct measurements of air–sea gas exchange rates in mesocosm experiments using N₂O as a tracer. N₂O is a perfect choice as a gas tracer in this application, due to its well known atmospheric concentration, relatively simple detection and structural similarity to CO₂. Although N₂O is not an inert gas, conditions favouring its biological production are unlikely to occur in pelagic mesocosms. Possible bias by biological activity is assessed by parallel measurement of natural variations in N₂O and will be discussed later in the manuscript. The conversion of measured N₂O exchange rates to those of CO₂ 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 Ocean Simula-

tion, Fig. 1) 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 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 CO₂ treatment concentrations were achieved through addition of CO₂ saturated seawater. While the ambient (~ 180 μatm *p*CO₂) control treatment was replicated twice, the seven enriched mesocosms followed a gradient up to ~ 1420 μatm *p*CO₂. Development of the enclosed natural plankton community was followed for 30 days after CO₂ manipulation, including addition of inorganic nutrients on day 13. For more details see Riebesell et al. (2012) and Schulz et al. (2013).

2.2 N₂O addition

One litre of saturated N₂O solution (N₂O medical, Air Liquide, purity > 98 %) was prepared via bubbling of seawater for two days in a narrow measurement cylinder covered with Parafilm[®]. Amounts of the solution to be added to the mesocosm were calculated using solubility constants by Weiss and Price (1980) with respect to in situ salinities (*S*) and temperatures (*T*). The targeted concentrations of N₂O 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 certified reference material for N₂O analyses available in our lab (~ 55 nmol kg⁻¹).

Assuming a background concentration of 13 nmol kg⁻¹, 40 nmol kg⁻¹ of medical grade N₂O 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 mL m⁻³) can be calculated according to the formulation:

$$V_{\text{ad}} = \frac{V_{\text{w}} \cdot \text{ad}}{K_{TS} \cdot p}, \quad (1)$$

where V_{ad} is the volume of N₂O stock solution added (L), V_{w} the volume of the mesocosm (L), ad the desired addition (mol L⁻¹), and K_{TS} is the solubility constant by Weiss and Price (1980) for *S* and *T* of the N₂O stock solution (mol L⁻¹ atm⁻¹) prepared at a pressure, *p* (atm), of one atmosphere.

A syringe with a large inlet diameter was used to transfer the stock solution carefully. Filling of the syringe was done

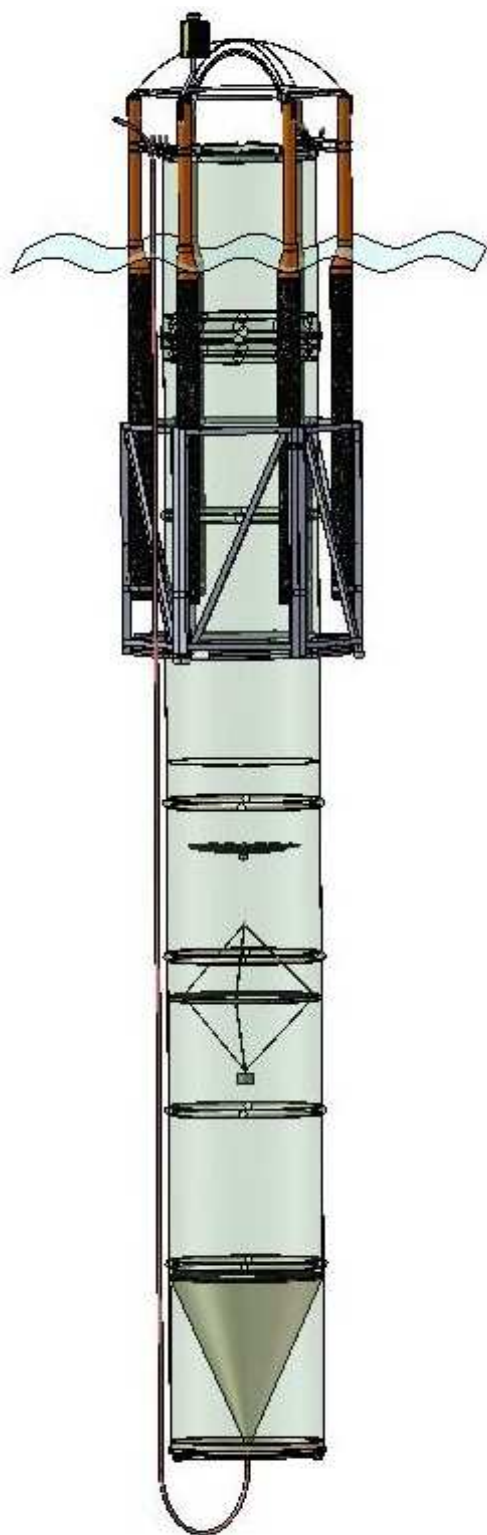


Fig. 1. Drawing of a KOSMOS mesocosm in the configuration used for the Svalbard experiment.

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 rim. The content of the carboys was homogeneously distributed to the mesocosms by using the pumped injection device “Spider” (Riebesell et al., 2012).

2.3 Sampling

Three of the nine mesocosms were sampled every second day using integrating water samplers (IWS, Hydrobios). Equal amounts of sample were sucked into the sampling bottle at each depth between 0 and 12 m, electronically controlled via hydrostatic pressure sensors. These integrated water samples represent inventories of the 15 m deep water column. Triplicate samples 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 (N 20, Machery and Nagel), crimp sealed and stored at room temperature after addition of 50 μ L of saturated mercury chloride solution.

2.4 Measurement procedures

Measurement of aquatic N_2O concentrations was performed via gas chromatography (GC) with electron capture detection (Hewlett Packard 5890 II), using a headspace static equilibration procedure as described by Walter et al. (2006, precision $\sim \pm 1.8\%$). The GC was equipped with a $6'1/8''$ stainless steel column packed with a 5 Å molecular sieve (W. R. Grace & 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 to the sample vials and later injected into the sample loop of the GC after equilibration was achieved by manual shaking and storage of the vials for at least 10 h at a temperature of 21 °C. Certified gas mixtures of N_2O in artificial air (Deuste Steininger GmbH) with mixing ratios of 87.2 ± 0.2 , 318 ± 0.2 and 1002 ± 0.2 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.

Total dissolved inorganic carbon (CT) was determined via coulometric titration using a SOMMA system and total alkalinity (TALK) via potentiometric titration (Dickson, 1981) (standard error of both methods $\sim \pm 1 \mu\text{mol kg}^{-1}$). CO_2 concentrations, partial pressures and pH (total scale) were calculated from CT 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 $\sim 0.2 \text{ g kg}^{-1}$ 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 Alesund.

Atmospheric measurements of N_2O and CO_2 were measured on close by Zeppelin Mountain ($\sim 4.5 \text{ km}$ from the experimental side) and provided to us by the NOAA Carbon Cycles Gases Group in Boulder, CO, USA and ITM in Stockholm University, Sweden, for N_2O and CO_2 , respectively.

3 Results and discussion

Concentrations of N_2O added on day 4 decreased in the enriched mesocosms from initially measured $\sim 50 \text{ nmol kg}^{-1}$ on day 6 to $\sim 30 \text{ nmol kg}^{-1}$ on day 28 (Fig. 2). 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 a standard diffusion relationship:

$$C_{\text{N}_2\text{O}} = 60.556 \cdot e^{-0.0241 \cdot d} \quad (2)$$

where the concentration of N_2O ($C_{\text{N}_2\text{O}}$) is described as an exponential function of the sampling day (d).

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 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$ ($F_{\text{N}_2\text{O}}$) across the water surface according to

$$F_{\text{N}_2\text{O}} = \frac{I_{w1} - I_{w2}}{A \cdot \Delta t} \quad (3)$$

where I_{w1} is the fitted bulk water N_2O inventory in μmol per mesocosm on t_1 and I_{w2} 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 ($k_{\text{N}_2\text{O}}$) in cm h^{-1} is then calculated by dividing $F_{\text{N}_2\text{O}}$ by the concentration gradient according to Eq. (4):

$$k_{\text{N}_2\text{O}} = \frac{F_{\text{N}_2\text{O}}}{(C_{\text{N}_2\text{O} \text{ w}} - C_{\text{N}_2\text{O} \text{ aw}})} \quad (4)$$

where $C_{\text{N}_2\text{O} \text{ w}}$ is the fitted bulk water N_2O concentration ($\mu\text{mol cm}^{-3}$) at the point in time and $C_{\text{N}_2\text{O} \text{ aw}}$ the calculated (Weiss and Price, 1980) equilibrium concentration of N_2O

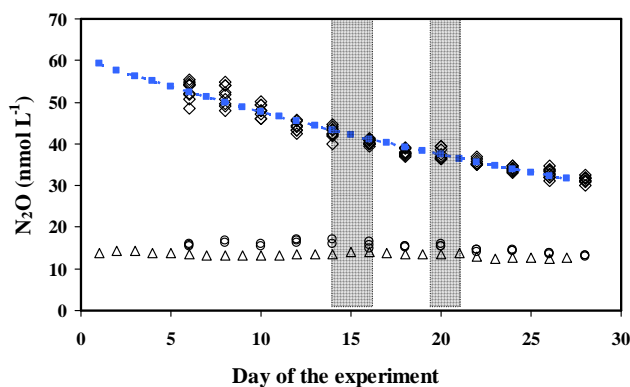


Fig. 2. N_2O concentrations during the experiment. Diamonds (\diamond) represent the measured concentration inside the three examined mesocosms; blue squares (\square) are fitted daily concentrations according to equation 2, circles (\circ) are background N_2O concentrations measured in the surrounding fjord, triangles (\triangle) are calculated equilibrium concentrations from atmospheric measurements at in situ T and S . Shaded areas indicate periods when waves (up to $H_{1/3} = 0.8 \text{ m}$) occurred at the mooring site.

with the atmosphere at prevailing bulk water T and S . Using bulk water concentrations to derive a surface diffusion gradient perfect mixing of the mesocosm appears to be an absolute requirement. Referring from N_2O to inert gasses with air–sea gas exchange being the only exchange process, it is irrelevant whether exchange is limited by mixing processes close to 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 cannot 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. Here, N_2O and CO_2 inventories have to be determined by integrated water samples independently from surface gradients determined from discrete surface water samples. Regardless of the specific sampling strategy applied, it is imperative to use the same protocol for the tracer as for the gases of interest.

Due to convection caused by slight temperature changes in the surrounding water (Fig. 5) and an evaporation induced salinity increase (Schulz et al., 2013), the mesocosms in the Svalbard KOSMOS study could be considered to be homogeneous on time scales relevant for air–sea gas exchange. N_2O as well as CO_2 surface concentrations are therefore adequately represented by bulk water measurements.

$k_{\text{N}_2\text{O}}$ 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 CO₂ (k_{CO_2}) in Eq. (5):

$$k_{\text{CO}_2} = \frac{k_{\text{N}_2\text{O}}}{\left(\frac{S_{\text{cCO}_2}}{S_{\text{cN}_2\text{O}}}\right)^{0.5}} \quad (5)$$

The Schmidt number for N₂O ($S_{\text{cN}_2\text{O}}$) published by Rhee (2000), and the Schmidt number for CO₂ (S_{cCO_2}) derived from diffusion coefficients published by Jähne et al. (1987) were used. Using this pair of Schmidt numbers, k_{CO_2} is generally less than 1 % smaller than $k_{\text{N}_2\text{O}}$, similarly to when both Schmidt numbers are derived from coefficients published by Jähne et al. (1987). If both coefficients are taken from Wilke and Chang (1955) the difference is ~ 10 % and can become larger than 25 % if S_{cCO_2} from Wilke and Chang (1955) is paired with ($S_{\text{cN}_2\text{O}}$) derived from coefficients published by Broecker and Peng (1974). More recent wind and wave tank experiments have shown that a conversion of $k_{\text{N}_2\text{O}}$ to k_{CO_2} is not necessary as gas exchange of the two gases is indistinguishable under conditions where chemical enhancement of CO₂ exchange is not relevant (Degreif, 2006). Fluxes for CO₂ (F_{CO_2}) can then be calculated by multiplication of k_{CO_2} with the diffusion gradient between bulk water CO₂ concentrations ($C_{\text{CO}_2\text{w}}$) and calculated equilibrium concentrations with the atmosphere ($C_{\text{CO}_2\text{aw}}$) as

$$F_{\text{CO}_2} = k_{\text{CO}_2} \cdot (C_{\text{CO}_2\text{w}} - C_{\text{CO}_2\text{aw}}). \quad (6)$$

Daily CO₂ fluxes were calculated for the nine mesocosms within the Svalbard ocean acidification experiment (Fig. 3). In the first days after CO₂ addition was completed (day 4), maximum efflux of ~ 2 μmol CO₂ per kg seawater and day could be observed in the highest CO₂ treatment (~ 1400 μatm) at a CO₂ gradient of ~ 980 μatm. In the following two weeks, the CO₂ gradient was diminished by outgassing CO₂ in concert with biological uptake, so that fluxes on day 27 were considerably lower (gradient ~ 450 μatm). Decrease of fluxes as a result of decreasing CO₂ gradients was less pronounced in the more moderately oversaturated mesocosms due to a higher buffer capacity of the carbonate system. About 0.5 μmol kg⁻¹ d⁻¹ CO₂ gassed into the water from the atmosphere in the non-manipulated control treatments (~ 175 μatm). Here, biological uptake was roughly balanced by influx so that the gradient remained rather constant over time.

3.2 Chemical enhancement of CO₂ air–sea gas exchange

Another correction has to be applied to derive accurate CO₂ fluxes in calm environments like the KOSMOS mesocosms. As CO₂ reacts with water, unlike N₂O, CO₂ gas exchange might be chemically enhanced due to buffering of diffusive concentration change by equilibration reactions within the boundary layer. Other than inert gases, CO₂ diffuses

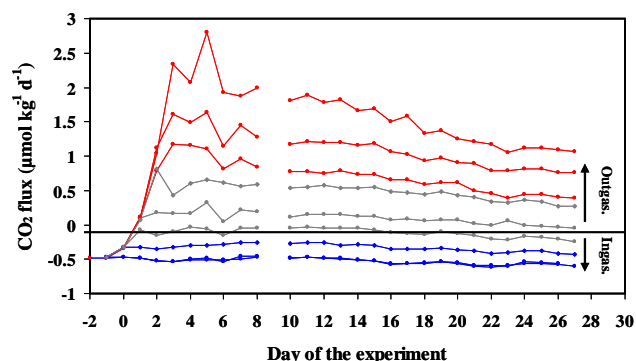


Fig. 3. Daily CO₂ fluxes for all CO₂ treatments over time. High CO₂ treatments are shown in red, medium in gray and low CO₂ are blue. Estimates include chemical enhancement according to Hoover and Berkshire (1969).

are not necessarily exchanged through the boundary layer, but can also be formed from bicarbonate close to the interface. This applies only at low wind speeds and not when mixing is considerably faster because CO₂ hydration kinetics are slow. Thus, chemical enhancement is thought to be rather insignificant under turbulent conditions relevant for open-ocean CO₂ exchange (e.g. when $k > 5 \text{ cm h}^{-1}$), but applies to the conditions found inside the mesocosms ($k \sim 1.8\text{--}2.5 \text{ cm h}^{-1}$) (Wanninkhof and Knox, 1996). Moreover, the state of the carbonate system determines the extent of chemical enhancement, being negligible at pH < 6 and substantial at 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 and Knox, 1996). The enhancement factor α , the ratio between chemical enhanced flux and not enhanced flux can be calculated using Eq. (7):

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

Here, dimensionless $\tau = 1 + [H^+]^2 (K_1^* K_2^* + K_1^* [H^+])^{-1}$, with K_1^* and K_2^* being the first and second stoichiometric equilibrium constants for carbonic acid and $[H^+]$ the proton concentration. $Q = (r\tau D^{-1})^{0.5}$ in cm⁻¹, where D is the diffusion coefficient for CO₂ by Jähne et al. (1987) and r describes the hydration of CO₂ either directly or via true carbonic acid. r in the unit s⁻¹ can be calculated using Eq. (8):

$$r = K_{\text{CO}_2} + K_{\text{OH}^-} K_{\text{w}}^* [H^+]^{-1} \quad (8)$$

with K_{CO_2} being the CO₂ hydration rate constant (s⁻¹), K_{OH^-} is the CO₂ hydroxylation rate constant (L mol⁻¹ s⁻¹)

from Johnson (1982) and K_w^* is the equilibrium constant for water. The boundary layer thickness z (cm) can be calculated from determined transfer velocity ($z = Dk_{\text{CO}_2}^{-1}$). 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 ($T = 5^\circ\text{C}$, $S = 35$, $z = 0.002$ 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 Quinn and Otto (1971), Emerson (1975), Smith (1985), and Keller (1994) give very similar results to the Hoover and Berkshire (1969) model (Wanninkhof and Knox, 1996). Experimental data from tank experiments reproduce calculated chemical enhancement relatively well (i.e. Hoover and Berkshire, 1969; Liss, 1973; Wanninkhof and Knox, 1996; Degreif, 2006). The simple pH dependent 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 open-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. 7). The influence of about three degree warming during the experiment in June 2010 is overall larger than the calculated difference arising from pH treatments (Fig. 4). Wrong pH-dependent chemical enhancement could produce artificial treatment effects in the carbon budget estimates especially in warm water ocean acidification studies. NCP estimates within this experiment 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 where temperatures are high, the proportion of CO_2 exchange relying on theoretical considerations is high compared to the directly measured flux.

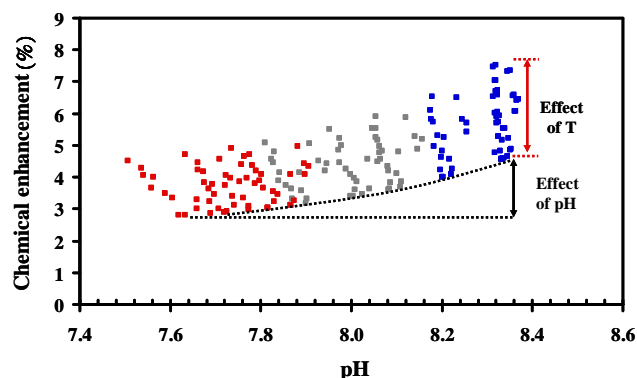


Fig. 4. Chemical enhancement of CO_2 compared to N_2O according to Hoover and Berkshire (1969) calculated for measured k , S , T and pH_{tot} during the Svalbard experiment. High CO_2 treatments are red, medium are gray and low CO_2 are blue. The effect of pH_{tot} on chemical enhancement is indicated by the black arrow, while the effect of the $\sim 3^\circ\text{C}$ temperature increase during the experiment is indicated by the red arrow.

3.3 The choice of N_2O as a gas exchange tracer and its biological stability

The N_2O molecule strongly resembles CO_2 in most physical properties; it has the same mass, nearly the same solubility and diffusivity. Other than CO_2 , equilibrium reaction of N_2O with water lies strongly on the side of free N_2O so that air–sea gas exchange can be approximated as for inert gases. In laboratory experiments N_2O is a perfect tracer for CO_2 gas exchange. Because of the similarity of both gases a conversion of measured $k_{\text{N}_2\text{O}}$ to k_{CO_2} is small and so are potential uncertainties. Wall effects relevant in laboratory experiments such as permeability or adhesion to plastic walls can be assumed to be comparable between similar molecules. In open waters, background concentrations of N_2O are slightly variable. Therefore, ^3He and SF_6 were used as gas exchange tracers in open-ocean applications as they are highly inert, their natural background concentration and detection limit is very low so that measurement is possible also after considerable dilution. Despite many practical advantages of N_2O in the application in mesocosms its prominent role as a biologically produced climate relevant trace gas is putting the inertness of N_2O into question.

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 significant 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 also be a source

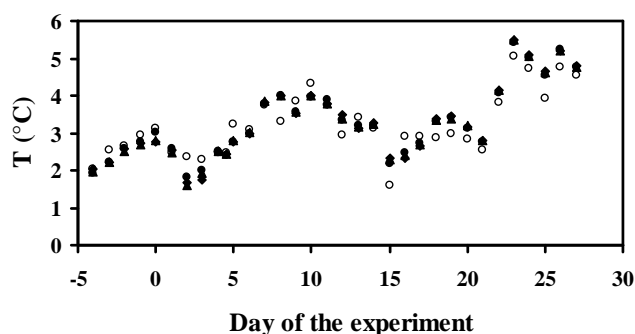


Fig. 5. Mean water temperatures between 0–12 m measured during the Svalbard experiment. The three examined mesocosms are shown as black symbols, while open circles represent measurements from the surrounding fjord.

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 N_2O production at relatively high surface layer nitrification rates, as found in upwelling regions (Rees et al., 2011), are orders of magnitudes too low to significantly bias the large fluxes caused by deliberate N_2O addition. The only known pathway of biological N_2O uptake as a reactive nitrogen species is by denitrifiers at anoxic conditions ($< \sim 10 \mu\text{mol O}_2 \text{ kg}^{-1}$) (Zumft, 1997; Zamora et al., 2012). Conditions favouring this process are unlikely to form in mesocosms and would result in a loss of the tracer (as N_2) but not into utilisation of N_2O as a nitrogen source. Side-effects of N_2O addition on biological activity in mesocosm experiments can therefore not be expected. 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.

3.4 Lateral gas exchange by diffusion through mesocosm wall material

Gas fluxes through the mesocosm walls can be calculated if temperature dependent permeability coefficients of the foil material and gases of interest are known.

Fluxes through the wall (F_{wall}) in mol d^{-1} can be derived using the equation:

$$F_{\text{wall}} = \frac{D_t \cdot \Delta p \cdot A \cdot t}{z_m} \quad (9)$$

Here D_t is the permeability coefficient at a given temperature in $\text{mol} \cdot \mu\text{m atm}^{-1} \text{ m}^{-2} \text{ d}^{-1}$, Δp is the partial pressure difference between inside and outside in atm, A is the submerged

surface of the mesocosm walls in m^2 , t is the duration in days and z_m is the thickness of the material in μm . Turbulence of the media in and outside the mesocosm is not relevant to this diffusion gradient as permeation of the materials is generally orders of magnitude slower than removal and advection of gases in the media.

Estimates of lateral gas exchange for the Svalbard experiment were calculated based on permeability coefficients published for Desmopan[®] 385, (Bayer). Desmopan[®] 385 is the raw material of our bag foil (Walopur[®], Epurex Films). Direct measurements for Walopur[®] are not available for CO_2 and N_2O . Permeability for the specific temperatures was extrapolated.

For the experiments in the KOSMOS mesocosms, the fraction of the measured gas flux due to permeability of the bag material was maximal on the order of 1–2%. Fluxes are low because of the relatively thick foil (0.5 to 1 mm) at comparatively low temperatures. In the perspective of CO_2 gas exchange estimates for carbon mass balance it is generally not interesting whether CO_2 exchanges through the walls or via the water surface. However, differences between N_2O and CO_2 in the material specific permeability of the bags have the potential to cause systematic errors if exchange is largely through the foil and not with the atmosphere. 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 (27.1 and $51.7 \text{ mol} \cdot \mu\text{m atm}^{-1} \text{ m}^{-2} \text{ d}^{-1}$ for CO_2 and N_2O at 25°C , respectively) (Bayer MaterialScience, TPU TechCentre). For the Svalbard experiment bias through lateral gas fluxes were not corrected, as the overall magnitude of these fluxes was negligible. The data basis in terms of permeability measurements would not have allowed for an exact correction of such bias. A set of permeability measurements at a relevant temperature range would improve gas exchange estimates especially at temperatures above 10°C . 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 $k_{\text{N}_2\text{O}}$ is translated into transfer velocities of poorly water soluble gases, dissolution and adhesion of those gases in and on the plastic material could cause a lateral sink of these substances in addition to the permeability issue.

3.5 Sensibilities of the results towards uncertainties in measured variables

Sensitivities of the overall resulting CO_2 fluxes to uncertainties in the determination of the most important measured variables for the presented method were estimated (Table 1). Water temperatures are used on numerous occasions for the calculation of gas exchange rates, e.g. for the calculation of CO_2 from CT and TALK, for Schmidt numbers, for solubility

Table 1. Sensitivities of the overall resulting CO₂ fluxes to uncertainties in the determination of the most important measured variables of the presented method. The effect of systematic N₂O underestimation was tested using an alternative fit including only upper end values from the Svalbard dataset. The influence of errors in CO₂ gradient determination is denoted for an intermediate gradient of 400 µatm.

Parameter	Uncertainty in parameter	Uncertainty in CO ₂ fluxes
Sea surface temperature	±1 °C	±3 %
Mesocosm volume	±1 %	±1 %
Mesocosm surface	±1 %	±1 %
Systematic error in N ₂ O measurement	Outliers due to losses during sampling	0.26 ± 0.29 %
Air–sea CO ₂ gradient	±2 µmol in CT and TALK	±5 %

and chemical enhancement. Errors in k_{CO_2} , in response to uncertainties in temperature, are mainly caused by the temperature dependence of N₂O solubility. Errors in resulting CO₂ fluxes are largely balanced by errors in CO₂ solubility calculated using identical temperatures. The remaining sensitivity of 3 % for 1 °C appears to be relatively low in respect of usually very precise temperature measurements using current technology. It has to be kept in mind that gas exchange is a continuous process; therefore, measurement frequency should be adequate for sufficient description of relevant temperature changes during the entire duration of the experimental duration. At water temperatures above 10 °C, chemical enhancement corrections become important so that precise temperature records gain additional relevance. Uncertainties in mesocosm volume or surface area translate directly into errors in calculated CO₂ fluxes (one to one %) when k_{CO_2} measured in one mesocosm is applied to calculate gas exchange in a parallel mesocosm with different volume or surface area. A random uncertainty in N₂O determination of 1.8 % as denoted by Walter et al. (2006) would be averaged out due to the large number of fitted measurements. However, a hypothetical systematic underestimation of N₂O by including outliers possibly caused by N₂O losses from oversaturated samples would influence k_{CO_2} . The effect of systematic N₂O underestimation was tested using an alternative fit including only upper end values. Resulting CO₂ fluxes differ by 0.7 % in the beginning of the experiment when N₂O concentrations were high and roughly equal fluxes calculated including all N₂O measurements at the end of the experiment. Maximum uncertainties in CO₂ fluxes of 5 % due to errors in the determination of air–sea CO₂ gradients are calculated on the basis of a maximum uncertainty of ±2 µmol kg⁻¹ in CT as well as TALK and an intermediate CO₂ gradient of ~400 µatm. As absolute errors in CO₂ determination have to be seen in relation to the air–sea gradient, percentile errors are small

when gradients are large and vice versa. The effects of random errors in CO₂ determination on uncertainties in cumulative CO₂ mass flux over time are averaged out over time. A cumulative error of the applied constants cannot be given but it has to be highlighted that this is an additional source of uncertainty. Parameterisations of Schmidt numbers, solubility and rate constants, as well as diffusion coefficients cited in the text, were chosen to the best of our knowledge.

3.6 Processes driving gas exchange in mesocosms

The concentration of N₂O ($C_{\text{N}_2\text{O}}$) decreased quite steadily over the whole experimental period (Fig. 2). This indicates that N₂O 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 (U_{10}) reported velocities of up to 5 m s⁻¹ during the experiment (Fig. 6). The water surface of the mesocosms, however, is sheltered from direct wind shear by the two meter high plastic walls of the bag (Fig. 1; Riebesell et al., 2012).

Fetch, the distance wind could act on the water surface, was dependent on wind direction (maximum of ~10 nm in the Kongsfjorden). Waves that were able to propagate through the mesocosms (significant wave height ($H_{1/3}$) up to ~0.8 m) 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 the days with waves could not be resolved by our measurements. However, CO₂ gas exchange inside the mesocosms was measured to be constantly about three times higher than calculated flux at zero wind as performed by Delille et al. (2005) (Fig. 7, stagnant film thickness calculated according to Smith, 1985, chemical enhancement according to Hoover and Berkshire, 1969).

Applying a quadratic wind dependent 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 U_{10} wind speeds at the experimental site were generally lower than this (mean 2.1 m s⁻¹), and accordingly calculated mean air–sea gas exchange was also lower outside in the fjord than inside the mesocosms. Compared to relevant open-ocean gas transfer, estimated mesocosm CO₂ transfer velocities between ~1.9 to 2.5 cm h⁻¹ in the Svalbard experiment are low. They are within a gray zone of baseline gas exchange where buoyancy fluxes and chemical enhancement contribute largely to gas exchange so that purely wind depended parameterisations are not applicable (Wanninkhof et al., 2009). Additional factors can be argued 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 air–sea surface renewal compared to open water. Slight temperature changes in the surrounding water mass were immediately

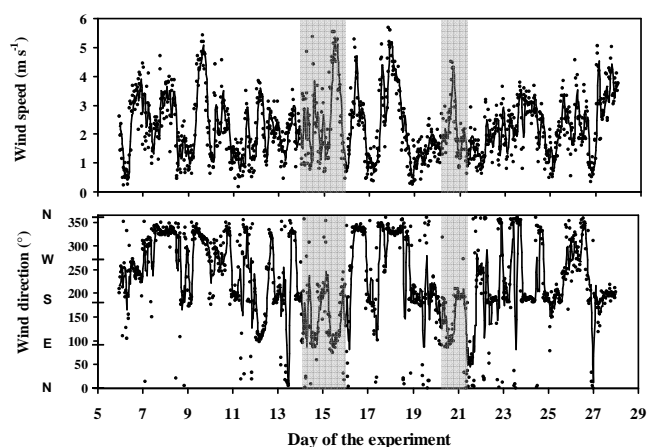


Fig. 6. Wind speed and direction during the course of the experiment, measured at 10 m height at Bayelva station, Ny Alesund. Waves (up to $H_{1/3} = 0.8$ m) were observed at the mooring site during time intervals indicated by shaded areas, when relatively strong wind was blowing along the fjord from southeast.

heating or cooling the bags (Fig. 5), this probably caused considerably enhanced buoyancy fluxes 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.

3.7 Mesocosm proportions

Transfer 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 15 m deep KOSMOS mesocosm (Fig. 1), holding $\sim 45 \text{ m}^3$ 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. 3). Taking the example of the Kiel indoor mesocosm (Fig. 8a) 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 20 times faster. Additionally, air–sea gas exchange velocities are accelerated by continuous active mixing, necessary to keep plankton organisms in suspension (Fig. 8a). While after 20 days $\sim 50\%$ of the N_2O added was still present during the Svalbard study (Fig. 1), the same tracer concentration was virtually gone after five days in the shallow indoor mesocosm (Fig. 8b) in the uncovered configuration. 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

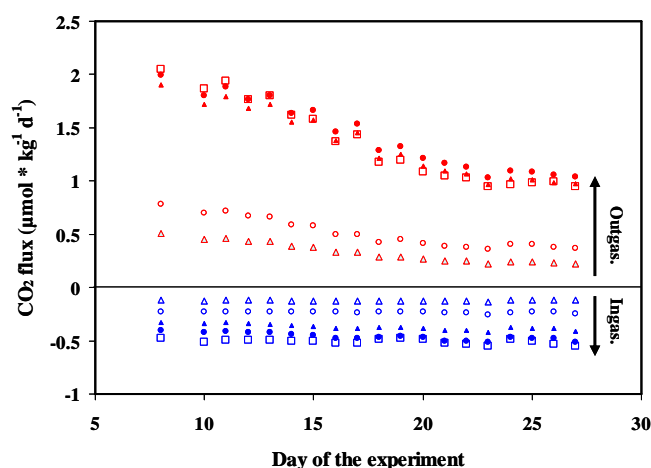


Fig. 7. Comparison of different approaches to estimate CO_2 air–sea gas exchange. Daily ingassing rates in the low CO_2 control treatment (average $\sim 180 \mu\text{atm}$) are shown in blue, while outgassing from the highest CO_2 treatment (average $\sim 1085 \mu\text{atm}$) is red. Filled symbols are estimates from the N_2O tracer approach, circles (\bullet) for chemical enhanced flux and triangles (\blacktriangle) for non chemical enhanced flux. Open squares (\square) 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 (\circ) are a chemically enhanced zero wind speed output, according to Smith (1985), while open triangles (\triangle) are the same estimate without chemical enhancement.

similar to the Kiel indoor mesocosm would lose their treatment CO_2 within a few days. To maintain treatment levels in such shallow experiments, continuous measurement and control technology can be used (see e.g. Widdicombe and Needham, 2007). 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. For comparison $50 \text{ nmol kg}^{-1} \text{ N}_2\text{O}$ was added to two Kiel indoor mesocosms, one in an uncovered configuration and one covered with a transparent floating foil to reduce surface in contact with the atmosphere (Fig. 8a). Both mesocosms were stirred at the same speed; samples were drawn using a tube. The thin polyurethane foil mounted on a light frame and floating on the surface, efficiently minimised air–sea gas exchange (Fig. 8b). 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. As the working principle of this approach is to minimise surface area, it can be assumed to be very sensible to the size of the remaining interface (leaks). Therefore, air–sea gas exchange should be measured in all experimental units to check for reproducibility of results.

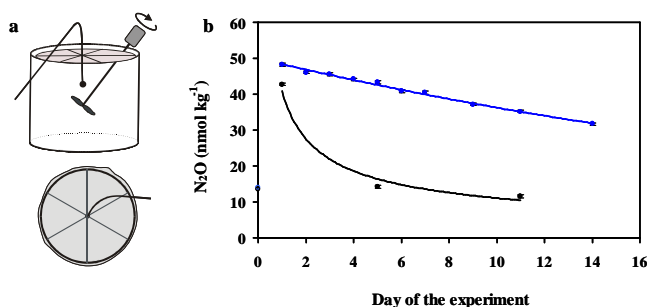


Fig. 8. (a) Schematic drawing of the Kiel indoor mesocosm. With stirrer, floating lid and sampling hose, below: vertical view on floating foil lid with enforcement frame. (b) Comparison of N_2O tracer outgassing in a Kiel indoor mesocosm, between a simple uncovered setup (black) and a setup using a floating foil lid reducing the water surface area available for air–sea gas exchange (blue).

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 wind dependent parameterisations for air–sea gas exchange cannot be adapted to mesocosm conditions and their application is therefore prone to systematic errors. Within the mesocosm low energy physical surrounding, N_2O gas exchange measurements allow for direct estimation of CO_2 fluxes with uncertainties far below open-ocean dual tracer measurements due to a known, constant water volume. Measured transfer velocities are within the range of zero wind open-ocean baseline velocities assumed to be dominated by chemical enhancement and buoyancy fluxes (Wanninkhof et al., 2009). 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 decrease in open-ocean k by 20–50 %, due to surfactants smoothening wind effects on the water surface (Tsai and Liu, 2003), can be expected to be of minor relevance to mesocosm gas exchange where wind stress is not the dominating energy input. The effect of these surfactants, possibly produced in high amounts during phytoplankton blooms in mesocosms, is difficult to include in theoretical calculations, but is inherently included in our direct measurements. Future mesocosm experiments combining the close observation of biological, chemical and physical processes might offer the opportunity to bring more light into origin and composition of organic surface microlayers.

The application of gas exchange measurements for calculation of NCP inside the mesocosm delivered satisfying results. 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., 2013; de Kluijver et al., 2013), comparability to ^{14}C incubation data presented by Engel et al. (2012) is weak. 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. ^{13}C tracer incorporation measurements inside the mesocosm deliver results representative for the entire mesocosm but only for a period before organic matter approached saturation with the tracer (de Kluijver et al., 2013). Rates measured in side experiments are more useful to compare community production between the treatments rather than giving quantitative cumulative estimates for in situ carbon uptake (see discussion in Engel 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 could 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, mesocosm NCP 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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